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The Rheology Of Silica Dispersions Taking Into Account The Genesis Of Quartz And Plasticizer Type

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Abstract- The rheological properties of composite binders are among the main ones during the design of composites on their basis. At that rheometry is an operational method of material quality estimation, as it allows to get the raw data in a short time, and to formalize many process steps and optimize their course, as well as to evaluate the system structure in a complex. The rheological and structural and mechanical properties of the mortar are shown in the process of its deformation, flow and decomposition. The results of these tests help to evaluate the possibility of a binder and superplasticizer use for a specific material. The hypothesis was put forward in this study concerning the effect of the phase and dimensional micro- and nanoheterogeneity of silica raw materials of different genetic types developed during the mechanical activation, and the chemical base of surfactant additives on the interaction in the system "silica - plasticizer" and "silica - plasticizer - cement" and, as the consequence, on the reotechnological characteristics of mortar and the physical and mechanical properties of fine-grained concrete. On the basis of the data obtained in the work the usefulness of plasticizer use for metamorphic quartz on polycarboxylate basis is demonstrated; for intrusive-magmatic quartz the usefulness of additives on the basis of melamine is demonstrated.

Keywords: genesis, rheology, plasticizer, silica, mechanical activation.

Introduction

Among numerous construction materials the binders are highlighted. The binders are the main carriers of material strength properties. Besides, the flow rate of a binder determines production costs. At that the properties of binders and the materials on their basis are directly dependent on the characteristics of mineral raw materials for their production. Due to this, the record of genetic, and, therefore, typomorphic characteristics of minerals for the production of various types of binders and composites on their basis may significantly reduce the energy consumption for their production and improve their performance properties.

The transition to composite binders, one of which is a binder of low water demand will allow to obtain high performance construction composites at the reduction of a cement share. In this regard, the proposition was put forward as a working hypothesis concerning the impact of a phase and dimensional micro- and nanoheterogeneity of silica raw materials of different genetic types formed during mechanical activation, and chemical basis of surfactant additives on the interaction in the composite binding system.

According to Russian and foreign literature, a number of scientific schools perform the studies to

analyze the influence of mechanical activation processes on the properties of the crushed material and its physical-chemical activity in different systems [1-9]. At that the works [2, 5, 7, 11] revealed that at the mechanical activation of quartz material the processes of amorphization of nanoscale particle surface layer and the occurrence of quartz crystals high-temperature modification take place. Silica raw materials of different genetic types are classified by the degree of mechanical activation effect on the change of its phase-dimensional heterogeneity in the following order: hydrothermal quartz → magmatogenic-intrusive → metamorphic (greenschist facies of metamorphism) [10-13].

Experiment method

In order to test the hypotheses regarding the influence of an additive chemical basis on the final properties of the materials several ways of plasticizer introduction were described at different stages of a composite binder (CB) production. The paper used joint and separate methods for the binder preparation. The joint grinding was performed on single-stage basis up to a specific surface of 500-550 m²/kg. The separate grinding was carried out in two stages: during the first stage the grinding of quartz component was performed up to specific surface area of 300-350 m²/kg, during the second stage the additional grinding with cement was performed. To s In order to study the effect of plasticizer on the additive grinding processes the additives were introduced at various stages of CB production. The selection of additives was performed by the method of mini cone. In order to confirm the hypothesis the properties of suspensions "silica

component - water", "silica component - surfactant - water" were studied. The rheology of silica dispersions using a rotational viscometer Rheotest RN4.1 obtained the values of an effective viscosity from the gradient shear rate. After the processing of the results, the curves of effective viscosity (η) dependence on the shear rate ($\dot{\epsilon}$) were developed.

The work used modifiers as the raw materials with a comparable plasticizing effect, but on different chemical bases: 1) melamine formaldehyde (MelmentF10); 2) polycarboxylate (FOX-8H); the quartz components of different genetic types: sand quartz of Korochansky field, quartzitic sandstone crushing sieve quartz from Lebedinsky GOK was used as an intrusive-magmatic type.

Results and discussion

The effect of quartz genetic type on the mobility of the system "cement - sand - plasticizer - water" (Fig. 1) was determined. When the binder based on silica component with high β -quartz (metamorphic quartz) content was used the maximum cone flow among the compounds based on polycarboxylate additive is achieved at the dose of 0.3%, which is 1.5 times lower in comparison with the dosage for a binder on the basis of silica component with a high content of α -quartz (intrusive-magmatic quartz). At that the cone flow for the binder based on both types of quartz with the use of the same polycarboxylate additives is similar. When the melamine formaldehyde additive is used an optimal dosage makes 0.6% regardless of the type of quartz, but the cone flow of the binder on the basis of intrusive magmatic quartz is 6.5% higher.

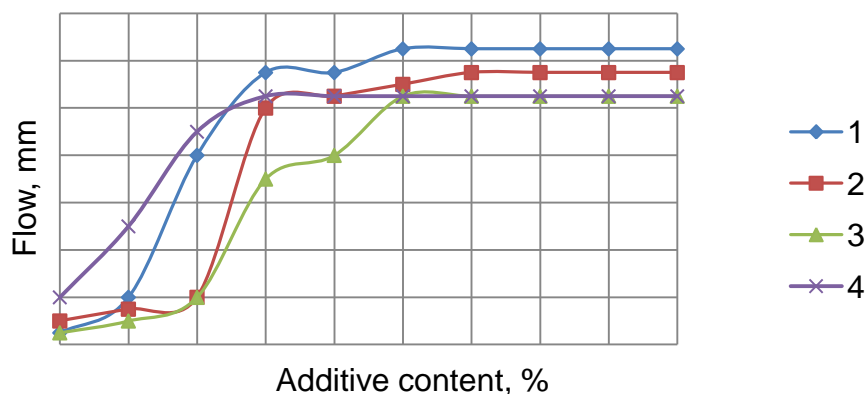


Fig. 1. The flow of TMTS-50 cone, depending on the type and amount of plasticizer based on different raw silica: intrusive magmatic quartz with melamine formaldehyde (1) and polycarboxylate (3) plasticizer; metamorphic quartz with melamine formaldehyde (2) and polycarboxylate (4) plasticizer

A substantial effect of a plasticizer type on the kinetics of quartz component grinding of different genetic type is noted (Fig. 2). Quartz of metamorphic origin is crushed to 30% faster than the intrusive-magmatic silica component. The grinding of a quartz component in the presence of a plasticizer is characterized by a steady trend towards dispersion

period reduction irrespective of additive and silica type. At that the co-grinding of a silica component and an additive reduces grinding period by 10% for intrusive-magmatic quartz with melamine formaldehyde plasticizer and by 30% for the metamorphic one with polycarboxylate one.

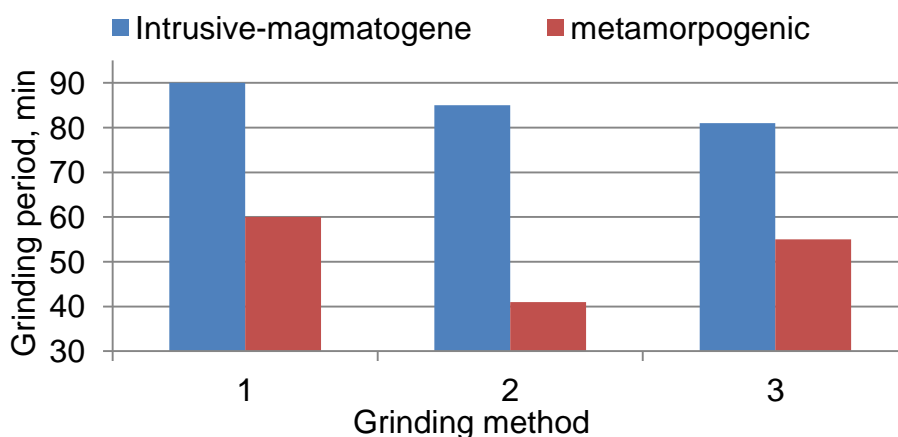


Fig. 2. Silica component grinding kinetics with plasticizers:
 1 - without plasticizer; 2 - with polycarboxylate;
 3 - with melamine formaldehyde

Analyzing the rheograms of quartz suspensions (Fig. 3), it should be noted that with the deformation rate increase the curves of all compositions are characterized by a thixotropic flow type typical for these systems, i.e. there is an even lowering of a suspension effective viscosity with a

quartz component and the increase of gradient shear rate value.

The suspension of metamorphic quartz crushed without a plasticizer, at a static voltage is characterized by a maximum viscosity which is conditioned by the formation of strong coagulation

structure due to the interaction between the particles in the "quartz - water" system. By applying a dynamic load to the system (gradient shear rate increase from 5

to 12 s⁻¹) the viscosity reduction is observed due to the gradual destruction of a suspension coagulation structure.

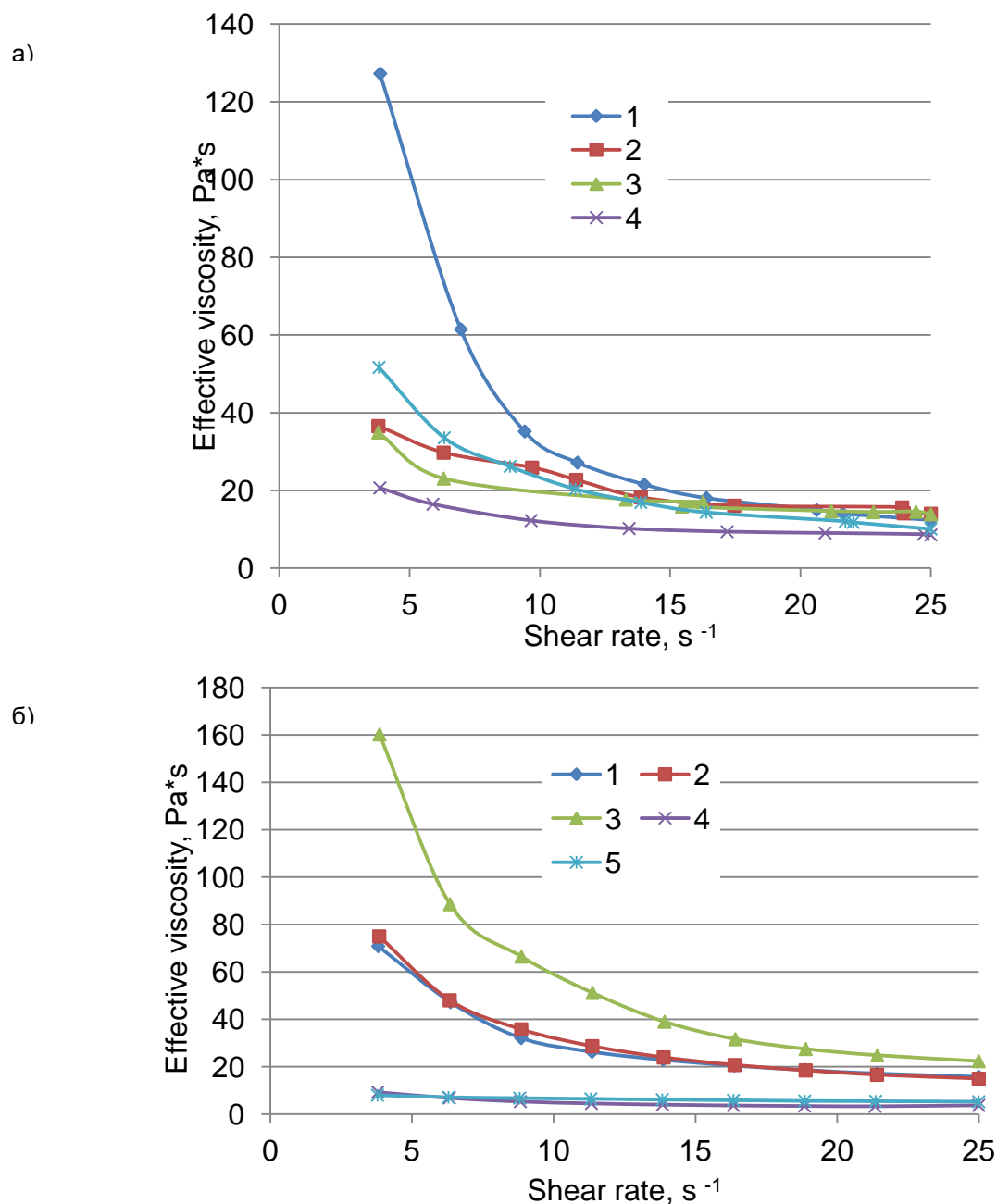


Fig. 3. Rheograms of metamorphogenic (a) and intrusive magmatic (b) quartz, depending on the type and the way of plasticizer introduction:

1, - ground quartz; 2 - quartz powder, together with FOX-8H; 3 - quartz powder, together with MelmentF10; 4 - ground quartz, mixed with FOX-8H; 5 - quartz powder mixed with MelmentF10.

The co-grinding of a quartz component and a plasticizer, regardless of its chemical base reduces the

initial viscosity of a system, however, the general character of the curve flow does not change. At that the

viscosity of suspensions obtained by co-milling of metamorphic quartz with a double additive for polycarboxylate plasticizer, and 1,5 additive for melamine formaldehyde as compared with the suspensions of mixed components.

A probable explanation for this behavior of the system is a number of factors. Primarily the presence in the system of plasticizer facilitates the crushing of quartz components, i.e. plasticizer acts as a dispersant. However, as was stated earlier, in the process of mechanical activation effect on the surface of silica component an amorphized shell is developed and a high-temperature modification of quartz takes place, which depends directly on genetic nature of quartz.

Metamorphogenic quartz is characterized by a high content of β -quartz and X-ray amorphous phase, which ensures its high reactivity compared with the intrusive-magmatic quartz. Consequently, the chemical sorption of plasticizer molecules takes place during their co-milling on the juvenile surface of a quartz component. Adsorption The adsorption of a plasticizer on silica particles leads to a reorientation of molecular additives, due to which the hydrophobization of a solid phase surface and, consequently, an increase of a system viscosity takes place. In the case of preliminary grinding of quartz and its subsequent mixing with a plasticizer, the suspending of a system results in the creation of conditions in which an additive reacts with water to form a solvation shell on the surface of ground silica component particles, thus, diluting the system.

At the double reduction of a plasticizer dose the character of suspension rheological properties does not change. However, it is worth noting that polycarboxylate plasticizer has the maximum diluting effect for the metamorphogenic quartz.

The suspensions of intrusive magmatic quartz are characterized by several other dependencies. Thus, the suspensions of magmatic quartz, crushed together with a plasticizer, regardless of its chemical basis, have a maximum initial viscosity. In this case, the plasticizer influence mechanism on the rheological properties of

the suspension is similar to that described above. However, due to the lower activity of the magma quartz conditioned by a lesser amorphized layer on the surface of the crushed particles the predominant influence in this case is presented by mechanical dispersion processes of the component due to the use of a plasticizer. In this regard, during the suspending of crushed magma quartz un the system an excess of a dispersed phase is developed and the lack of dispersion medium that increases the system viscosity.

The reduction of the system viscosity for the suspensions of intrusive magmatic quartz milled without plasticizer is explained by worse grinding of quartz and the lower activity of this silica component compared with the quartz of metamorphogenic origin.

It is worth noting a significant impact of a plasticizer dosage on the rheological properties of suspensions based on intrusive-magmatic quartz. The double reduction of polycarboxylate plasticizer amount reduces the viscosity of quartz suspensions obtained by combined grinding of a silica component and plasticizer 4 times, indicating the lack of a plasticizer for the quality dispersion of a quartz component. The reduction of melamine formaldehyde plasticizer dosage in a system does not change the system viscosity dependence on the composition and method of an additive introduction.

Summary

According to the received data, the change in the rheological properties depends on the genesis of a quartz component and the chemical basis of the plasticizing component and has an effect on the structural and mechanical properties of mortars.

Conclusion

Thus, the dependence of reotechnological performance in the "quartz - plasticizer - water" system on the genetic type of silica-containing raw materials, the chemical basis of a plasticizer and the way of dispersion obtaining is revealed. The expediency of the

following use is proved: metamorphic quartz together with polycarboxylate plasticizers, and for intrusive magmatic quartz with the additive on melamine formaldehyde basis. It was shown that the preliminary grinding of quartz with plasticizer up to $S_{\text{yn}} = 300 \text{ m}^2/\text{kg}$, followed by final grinding with cement (separate milling) allows to reduce the viscosity by 3.5 and 6 times, and also to reduce the grinding period of intrusive magmatic and metamorphic quartz by 10% and 30%, respectively.

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