Finely Ground Quartz Sand and Plasticizing Admixtures Influence on Rheological Properties of Portland Cement Paste

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The effect of finely ground quartz sand and plasticizing admixtures on yield stress, viscosity and dilatancy of cement pastes was investigated experimentally. The studies revealed that the addition of quartz sand up to 5 % of the cement without plasticizing admixtures reduces the yield stress of such cement paste, whereas higher content of quartz sand in the cement does not cause a further change in the yield stress of the cement paste. With the increase of plasticizing admixtures from 0.2 % to 1.0 % in the cement paste with quartz sand additive the yield stress of the paste decreases. When 5 % of the cement is replaced by quartz sand the viscosity of the cement paste without plasticizing admixtures slightly reduces, whereas the raising of quartz sand content up to 20 % does not have a further effect on the viscosity both at high and low shear rate. The quartz sand content up to 5 % slightly increases the cement paste dilatancy, whereas the replacement for 20 % cement does not change the dilatancy of the paste. The dilatancy of the cement paste increases with more quartz sand and different chemical composition plasticizing admixtures. The studies have proved that rheological parameters of the cement paste are affected by the percentage by weight of finely ground quartz in the cement paste and the particles shape of this additive.
Keywords: Portland cement, finely ground quartz, plasticizing admixture, yield stress, viscosity, viscometer, dilatancy.

1. INTRODUCTION

In recent years plasticizing admixtures of different chemical composition have been used for the preparation of cement mixtures, therefore quite a number of studies have been conducted to examine the effect of plasticizing admixtures on the main rheological parameters of cement pastes, namely the yield stress and viscosity. On the other hand, the combined effect of mineral and plasticizing admixtures on rheological properties and dilatancy of cement pastes and concrete mixtures has received far less attention. Such studies are important from the technological point of view as they would help to forecast the workability of cement mixtures and their flowability during pumping.

According to the shape of the rheological curve of structural systems, cement pastes among them, some groups of structural liquids are defined: Newtonian fluid, pseudoplastic fluid, dilatant fluid, Bingham fluid, plastically dilatant body and pseudoplastic body [1, 2]. Cement pastes and concrete mixtures are usually defined as Bingham fluids (systems); they have two main rheological characteristics – yield stress τ_0 and plastic viscosity η [3–5].

The research into rheological properties of cement pastes using a rotational viscometer with coaxial cylinders revealed that cement paste behaves as Bingham plastic fluid and may be characterized by shear stresses (Pa) and plastic viscosity (Pa·s). The previous studies revealed that the Bingham model, which is suggested for describing cement paste flow curves, is not correct. The flow curve of cement pastes is not straight line, as it is in Bingham model, but it becomes a curve when the share stress is increased [6–8]. This demonstrates that cement paste is characterized by dilatancy, i. e. the viscosity of the system increases with higher shear stresses. According to O. Reynolds, this increase in viscosity is caused by the growth in volume of the dispersive system because of the change of distribution of the phase particles, while some particles move in regard to other, and by relative decrease in the volume of dispersive medium [9].

H. Freundlich and H. Roder [10] described the mechanism of dilatancy using the experiment with quartz and starch water suspensions, where the volume concentration of solid particles per unit was $0.42 - 0.45$. When suspension flow rates are low, solid particles can slide against each other without any significant distortion of the system that causes the system to thicken. When suspension flow rates are high, the system structure is distorted and interacting particles form a more open structure. The dosage of liquid phase in the system decreases as a result of bigger hollow spaces between the particles and the system stiffens. The dosage of liquid phase is insufficient to reduce friction between solid particles. Dilatancy of disperse systems has not been researched completely as in many cases the nature of dilatancy remains unclear.

According to Sh. Ookawara and K. Ogawa [11], the linear increase in viscosity with the increase of velocity gradient in suspensions, where solid phase particles are of uniform size, is described as dilatancy. The increase in suspension's viscosity is in proportion to the square of the solid particle content by volume and shows that the

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system's viscosity and particle density are linearly dependent on the average particle diameter.

Various chemical admixtures are used in practise to adjust rheological properties of cement pastes and concrete mixtures. Plasticizers and superplasticizers change rheological properties of concrete mixtures [12, 13]. The efficiency of plasticizing admixtures depends on their chemical composition [14, 15].

Sodium silicate solution admixture $Na_2O \cdot nSiO_2$ contains nano structures, which stimulate the additional intra-atomic bonding and increase the viscosity of the liquid phase that assist the bonding of cement and aggregate grains, increase resistance to segregation and improve flowability of the cement paste [16–19]. Authors [20] have examined the combined effect of sodium silicate solution and plasticizing admixtures based on polycarboxylic polymers on rheological properties of cement pastes and determined that with the increase of sodium silicate solution content from 0.2 % to 2.0 % in the cement the flow curve of the paste changes from linear Bingham model to pseudoplastic material flow curve.

The authors [21, 22] determined that plasticizing admixtures, irrespective of their chemical composition, reduce the yield stress and viscosity of cement pastes, but also increase the dilatancy of the pastes. Air entraining admixtures have irrelevant effect on yield stress and viscosity, but they significantly reduce the dilatancy of the pastes. Stabilizing agents increase the yield stress of the pastes, have irrelevant effect on viscosity and reduce the dilatancy of the pastes.

Yield stress of cement paste goes down by increasing the dosage of dispersive additives; however the viscosity of the slurry changes depending on the additive type and content. According to the effect on the paste's yield stress, they may be classified as follows: blast furnace slag > limestone > silica fume > fly ash (10 % of the cement is substituted by these admixtures). When 35 % of blast furnace slag is added the paste's yield stress and viscosity are significantly reduced [23].

Ch. F. Ferarri, K. H. Obla and R. Hill researched the effect of different mineral additives and determined that fine fly ash particles had the biggest effect on reducing the yield stress and viscosity of cement pastes [24].

SiO_2 micro particles (silica fume) were found to increase the yield stress and viscosity in cement pastes with higher silica fume content. The dilatancy of the cement paste was mostly affected when the dispersive additive content in the cement was increased up to 5 %. Silica fume significantly reduces the dilatancy of the cement paste due to the fineness and spherical form of micro particles. SiO_2 micro particle suspension combined with plasticizing admixtures changes the dilatancy of the cement paste according to chemical composition of plasticizing admixture [25].

F. Cursio, B. A. De Angelis analyzed cement pastes with rotational viscometer, compared rheological properties of the paste with metakaolin and silica fume and determined that pastes with metakaolin possess less thixotropy, while silica fume increases the thixotropy of the paste [6]. Dilatancy is explained as the friction in suspension between contacting hard angular and flat metakaolin particles. Shear thickening behaviour depends on the rate of water and binding material, metakaolin content and fineness.

M. Cyr, C. Legrand, M. Mouret researched the effect of mineral admixtures on the dilatancy of the paste and determined that metakaolin increases the dilatancy of the paste, quartz and fly ash have no effect, while silica fume reduces the dilatancy of the paste [26].

According to the authors [27], active dispersive additives, due to their big specific surface area, increase the water content required to prepare the cement paste of required consistency. Active dispersive additives used together with plasticizing admixtures change diffusive properties of the adsorption layer of cement particles and accelerate hydration of the cement, however reduce the plasticizing effect on the cement paste.

J. Gallias and co-authors [28] analyzed the effect of granulometric characteristics of mineral additives (suspensions of finely ground quartz, dolomite, diatomite, kaolin, limestone and silica fume) on water demand in cement paste to obtain the required workability of the paste without using chemical admixtures which decrease the water demand. Cement paste water demand depends on the specific surface area (m^2/kg) of fine ground mineral additives used. In the opinion of the authors, mineral additives with broad particle size distribution may reduce the cement paste water demand.

The authors [29] state that cement paste's viscosity and yield stresses could be forecasted by using the exponential Mooney's equation, where the ratio, which depends on particle density in the paste, can be calculated from the volume concentration of normal consistency paste, while the acceptable particle form factor for Portland cement would be 2.7, and 2.9 for fly ash cement.

A. Sicker and co-authors [30], having analyzed the effect of different tuffs (silica fume suspension and metakaolin particles) and superplasticizers of different chemical composition on rheological properties of the cement paste, determined that viscosity rate of the cement paste with silica fume suspension and different plasticizers was lower compared to the viscosity rate of cement paste with metakaolin and the same chemical admixtures.

The purpose of this research was to analyze the effect of finely ground quartz sand and plasticizers of different chemical composition on rheological properties of cement pastes: yield stresses, viscosity and dilatancy.

2. MATERIALS AND METHODOLOGY

JSC "Akmenės cementas" (Lithuania) Portland cement CEM I 42.5 R was used for the test. Water demand for normal consistency Portland cement slurry – 27.5 %, specific surface area – 353 m^2/kg, particles density – 3110 kg/m^3, dry bulk density – 1220 kg/m^3.

JSC "Anykščių kvarcas" (Lithuania) finely ground quartz sand was used for the test. The finely ground quartz sand particles specific surface area – 255 m^2/kg, particles density – 2650 kg/m^3, dry bulk density – 1080 kg/m^3. Portland cement was replaced by finely ground quartz sand in range of 5 %–20 % of the cement mass (according the density of particles).

Three types of plasticizing admixtures were used in the tests, namely plasticizer L (produced by Klaipėda

celiuliozės fabrikas, Lithuania), superplasticizer SNF (pro-duced by REMEI Blomberg GmbH and Co, Germany) and superplasticizer PP (produced by BASF Construction Polymers GmbH, Germany). Plasticizer L based on ligno-sulphonates, is a liquid of the colour brown and containing 31 % of dry matter; density of the solution is 1.14 kg/l. Superplasticizer SNF based on naphtalenformaldehyde resin, is a liquid of the colour brown and containing 20 % of dry matter; density of the solution is 1.09 kg/l. Super-plasticizer PP based on polycarboxyl polymers, is a liquid of the colour ranging from light yellow to reddish brown and containing 30 % of dry matter; density of the solution is 1.11 kg/l. The plasticizing admixtures were mixed with water, used for preparation of the paste. The total dosage of admixtures was in the range from 0.2 % to 1.0 % of cement.

Cement and finely ground quartz sand particles shape and surface area microscopic tests were performed using a scanning electron microscope JSM-5600 (firm JEOL).

The cement slurry was mixed manually about 5 min. The cement was dosed by weight while water and chemical admixture were dosed by volume. Constant W/C ratio of 0.55 was maintained throughout the tests.

Rheological properties of the cement paste were determined by coaxial-cylinders rotational viscometer BCH-3; a simplified diagram and the principle of viscometer operation as well as methods of determining the rheological properties have been presented in the article [25].

3. RESULTS AND DISCUSSIONS

The flow curves of the cement paste (W/C = 0.55) with finely ground quartz (5 % – 20 % of the cement replaced with additive) are illustrated in Fig. 1.
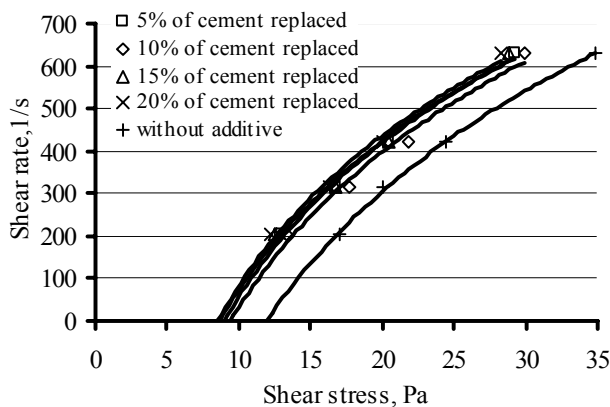

Fig. 1. Dependence of cement pastes shear rate on shear stress when finely ground quartz replaces Portland cement

The curves in this figure show that replacement of cement with finely ground quartz reduces the yield stress of the cement paste irrespective of the amount of quartz sand, compared to the paste without quartz sand aggregate. From the curve angle we may see that additive does not have a significant effect on the dilatancy of the cement paste as the arch of the flow curves does not change. According to authors [6 – 8] the flow curve of cement pastes is not straight line, as it is in Bingham model, but it

becomes a curve when the share stress is increased. This demonstrates that cement paste is characterized by dilatancy.

The flow curves of the cement paste (W/C = 0.55) with the same amount of plasticizing admixtures (0.6%) and different amount of quartz sand (5 % – 20%) are similar: the flow curves of the paste (quartz sand replaces 5 % – 20 % cement) with PP superplasticizer are more bent than the curves of the pastes with quartz sand and L plasticizer and SNF superplasticizer. PP superplasticizer has a bigger effect on the dilatancy of the cement paste than the additive content.

The flow curves of the cement paste with the same amount of finely ground quartz (10 %) and different amounts of varied chemical composition plasticizing admixtures are similar to the flow curves of dilatant mixtures: the flow curve of the cement paste, where 10% of the cement is replaced with finely ground quartz and no chemical admixture is added, is not linear either, as in Bingham's model, but has the shape of a curve (Fig. 1).
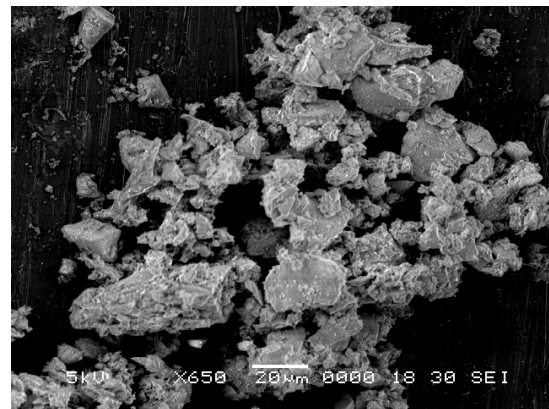

a
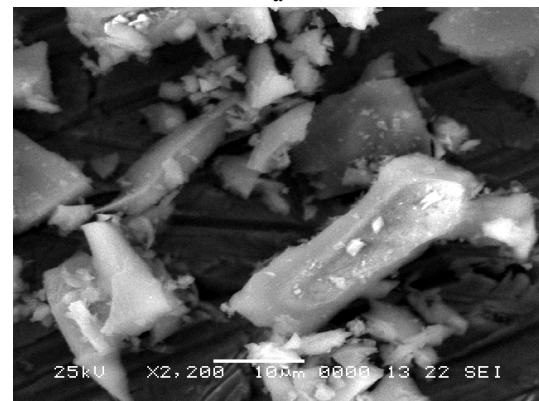
b

Fig. 2. Microscopy images of Portland cement particles (a); finely ground quartz particles (b)

The flow curves of the cement paste with the same amount of additive bend more when the amount of PP superplasticizer and SNF superplasticizer is increased. The angle of inclination of the flow curves shows that PP superplasticizer has a bigger effect than other chemical admixtures on the dilatancy of the cement paste.

Analysis of cement particles by scanning electron microscope showed that the edges of most Portland cement

particles are polished during grinding, therefore most of these particles have a shape similar to a cube or even a sphere (Fig. 2, a). This finding was made after random microscopic analysis of forty Portland cement particles, which diameter was about 3 μm – 60 μm. The results of microscopy tests (Fig. 2, b) show that finely ground quartz sand particles are of several microns in size, i. e. similar to the size of cement particles. The microscopy images also show that finely ground quartz sand particles have irregular shape, sharp edges and angles.

Fig. 3 illustrates the dependence of the yield stress on the additive content in the cement paste (W/C = 0.55) with finely ground quartz (replacement 5 % – 20% of cement). The figure shows that quartz sand added up to 5 % reduces the yield stress of the cement paste and has no further effect on the yield stress of the paste when higher content of quartz sand are used. X. Zhang and J. Han [23] obtained the same results that dispersive additives reduce yield stress of cement paste in different range according to additive type. The authors [23] stated the greatest effect of blast furnace slag. The particles shape of ground quartz sand the similar to particles shape of blast furnace slag and influence on yield stresses of cement paste is the same [29].
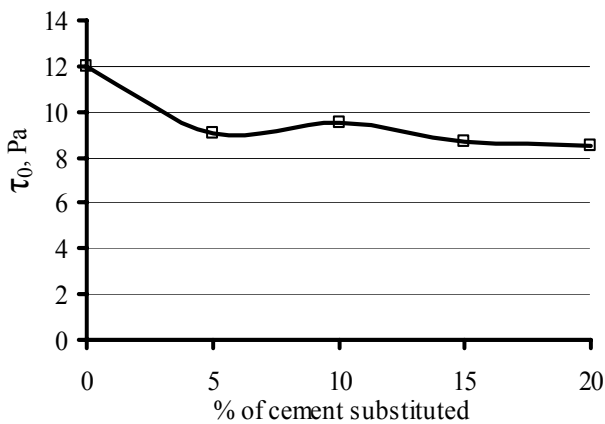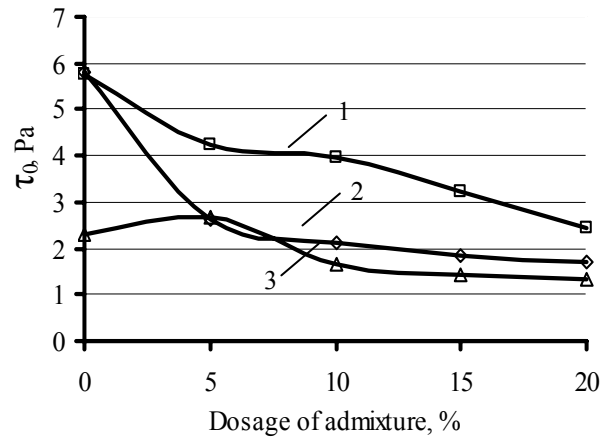

Fig. 3. Dependence of yield stress on the additive content in the cement paste where finely ground quartz replaces Portland cement

Fig. 4 illustrates the dependence of the yield stress on finely ground quartz content of the cement paste (W/C = 0.55) with plasticizing admixture (replacing 6 % of the cement). The figure shows that with the increase of quartz sand content from 5 % to 20 % in the cement and keeping the same content of plasticizing admixture (0.6 %), the yield stress of the paste reduces most when PP superplasticizer is used, and less with L plasticizer and SNF superplasticizer.
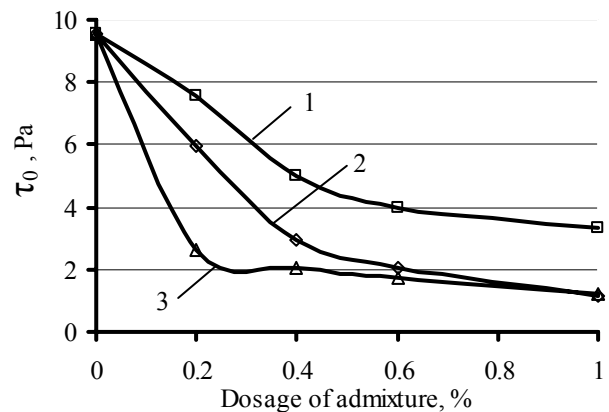
Fig. 5 illustrates the dependence of the yield stress on different amounts of plasticizing admixtures in the cement paste (W/C = 0.55) with the same amount of finely ground quartz (10 %).

The figure shows that with the increase of plasticizing admixture amount from 0.2 % to 1.0 % and with the same amount of quartz sand (10 %), the yield stress of the cement paste decreases. The biggest decrease in the yield stress is observed when PP superplasticizer and SNF superplasticizer are used, while with L plasticizer the yield

stress decreases less. PP superplasticizer based on polycarboxylic polymers has the biggest plasticizing effect on cement pastes. Most research results show the reduction the yield stress and viscosity of cement pastes by using various plasticizing admixtures [21, 22].

Fig. 4. Dependence of yield stress on finely ground quartz content in Portland cement paste: 1 – with L plasticizer; 2 – with SNF superplasticizer; 3 – with PP superplasticizer

Fig. 5. Dependence of yield stress on different amounts of plasticizing admixtures in Portland cement pastes: 1 – with L plasticizer; 2 – with SNF superplasticizer; 3 – with PP superplasticizer

Fig. 6 illustrates the dependence of viscosity on the amount of admixtures in the cement paste (W/C = 0.55) with finely ground quartz at velocity gradients of 205 s^{-1} and 630 s^{-1}. The figure shows that when 5 % of the cement is replaced with finely ground quartz the viscosity of the cement paste slightly reduces, however when the fine aggregate amount is increased up to 20 % of the cement, the viscosity of the paste does not change both at low and at high velocity gradient. Ch. F. Ferraris and co-authors obtained the same experimental results of cement pastes viscosity reduction using the fine fly ash particles like mineral additive [24].

Fig. 7 illustrates the dependence of viscosity on the amount of finely ground quartz in the cement paste (W/C = 0.55) with the same amount of plasticizing admixtures (0.6 %) at velocity gradients of 205 s^{-1} and 630 s^{-1}.

The figure shows that with the increase of quartz sand amount from 5 % to 20 % and the same amount of

plasticizing admixtures (0.6 %), the pastes viscosity reduces both at low and at high velocity gradient.
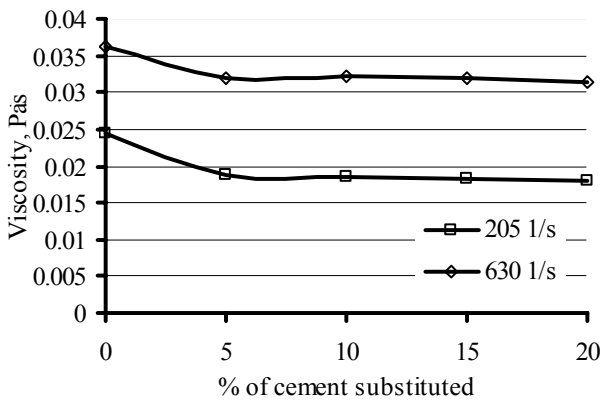

Fig. 6. Dependence of viscosity on the amount of additive in the cement paste at velocity gradients 205 s^{-1} (a) and 630 s^{-1} (b)

a

b

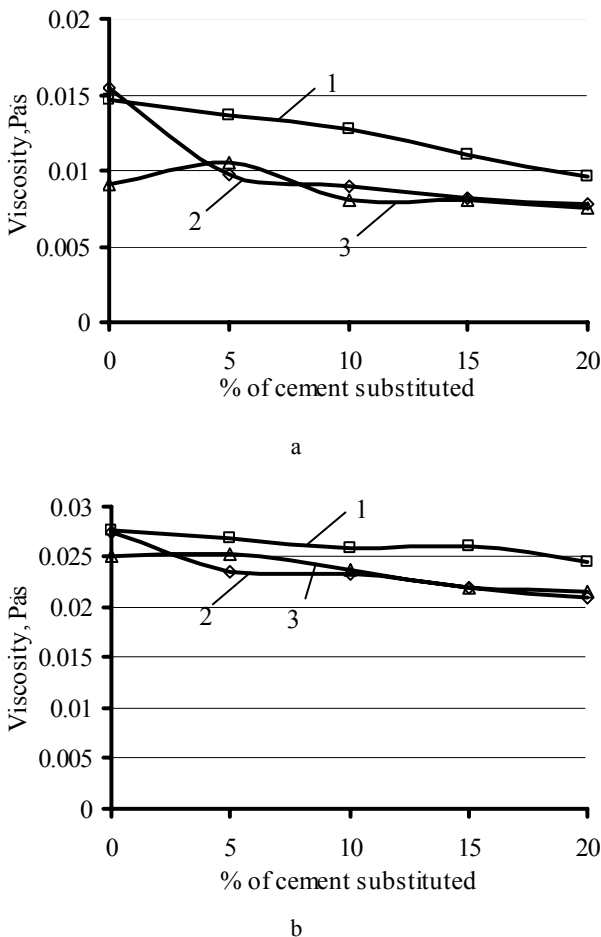**Fig. 7.** Dependence of viscosity on the amount of finely ground quartz in Portland cement paste at velocity gradients 205 s^{-1} (a) and 630 s^{-1} (b): 1 – with L plasticizer; 2 – with SNF superplasticizer; 3 – with PP superplasticizer

Fig. 8 illustrates the dependence of viscosity on different amounts of plasticizing admixtures in the cement paste (W/C = 0.55) with the same amount of finely ground quartz at velocity gradients of 205 s^{-1} (a) and 630 s^{-1} (b). The curves in the figure show that with the increase of the

amount of plasticizing admixtures from 0.2 % to 1.0 %, irrespective of their chemical composition, and the same amount of quartz sand (at 10 %), the pastes viscosity reduces both at low and at high velocity gradient. The authors [30] investigated complex usage of mineral additives with plasticizing admixtures. They determined better decreasing of viscosity of the cement paste with silica fume suspension and different plasticizers against with metakaolin. The fineness of finely ground quartz sand particles is much bigger mentioned mineral additives and viscosity of cement paste reduction with addition of ground quartz sand is not great.
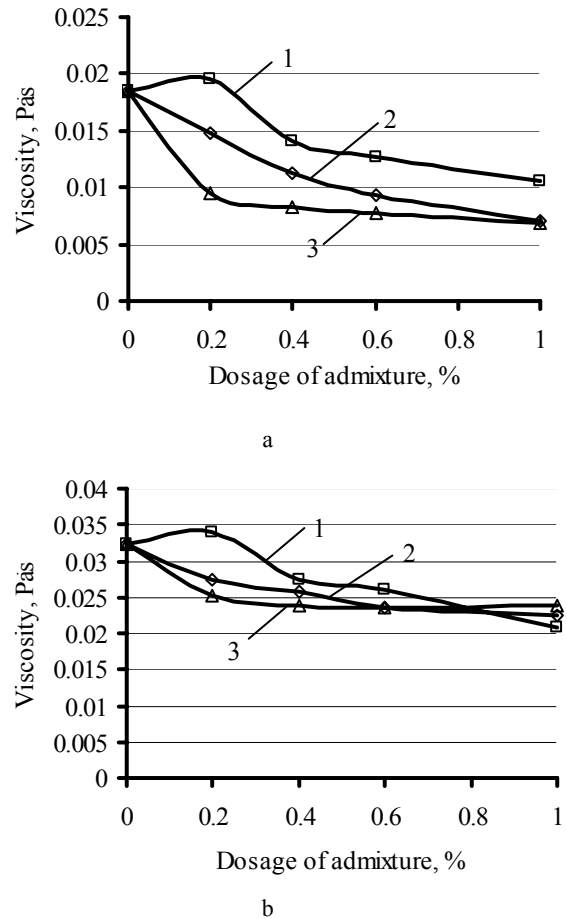

a

b

Fig. 8. Dependence of viscosity on different amounts of plasticizing admixtures in Portland cement paste at velocity gradients 205 s^{-1} (a) and 630 s^{-1} (b): 1 – with L plasticizer; 2 – with SNF superplasticizer; 3 – with PP superplasticizer

Fig. 9 illustrates the dependence of dilatancy rates D and D_1 on the amount of admixture in the cement paste (W/C = 0.55) with finely ground quartz. The dilatancy rate D shows the increase in cement pastes viscosity with the change of shear stresses at velocity gradients 205 s^{-1} and 630 s^{-1}. The dilatancy rate D_1 shows the increase in cement pastes viscosity with the increase in velocity gradient from 205 s^{-1} to 630 s^{-1}. Dilatancy is the increase in the systems viscosity at increasing shear stresses or flow rates, and the dilatancy of a mix is described by shear thickening behaviour.

The curves in Fig. 9 illustrate that finely ground quartz sand added up to 5 % slightly increases the dilatancy of the

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cement paste, while quartz sand added up to 20 % does not change the dilatancy of the paste. The increase in dilatancy of the cement paste resulting from finely ground quartz sand replacement for the cement can be explained by irregular form and angularity of quartz sand grains (Fig. 2, b). The above factors increase the friction of cement grains in the paste. The friction in suspension between contacting hard angular and flat particles F. Cursio, and B. A. De Angelis [6] explained the origin of dilatancy. Dilatancy depends on the ratio of water and binding material, mineral additive content and fineness. Conversely to the results obtained with the ground quartz sand according to authors [25] the silica fume significantly reduces the dilatancy of the cement paste due to the fineness and spherical form of micro particles. M. Cyr, C. Legrand and M. Mouret determined that metakaolin increases the dilatancy of the cement paste, quartz sand and fly ash have no effect, while silica fume reduces the dilatancy of the paste [26]. Sh. Ookawara and K. Ogawa [11] describe that the dilatancy is in great influence on solid phase particles of uniform size.
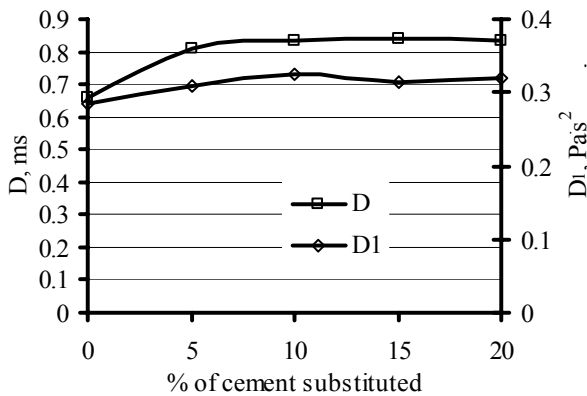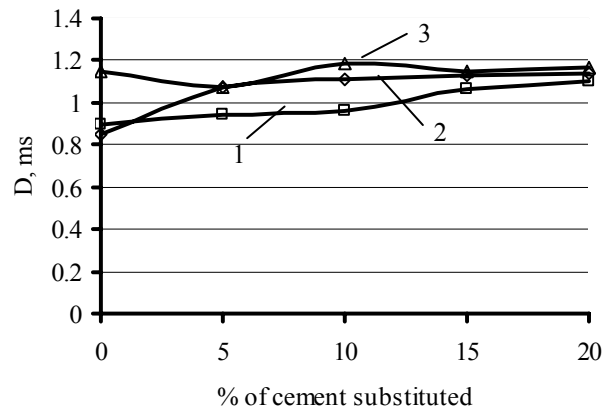

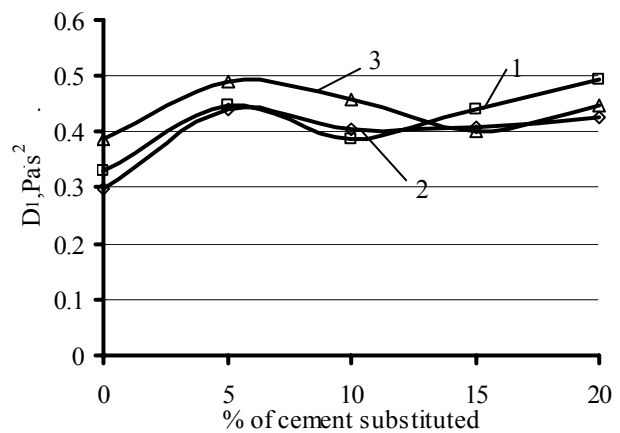**Fig. 9.** Dependence of dilatancy rates D and D_1 on the admixture content in the cement paste

Fig. 10 illustrates the dependence of dilatancy rates D and D_1 on the amount of quartz sand in the cement paste (W/C = 0.55) with the same amount of plasticizing admixtures (0.6 %). The curves in the figure show that with the increase of the amount of quartz sand from 5 % to 20 % and with the same amount of plasticizing admixtures, the pastes dilatancy rates D and D_1 increase when L plasticizer and SNF superplasticizer are used, and change very insignificantly when PP superplasticizer is used. PP superplasticizer has a bigger effect than additive on shear thickening behaviour of the cement paste. Finely ground quartz replacement for 5 % cement slightly increases the dilatancy of the cement paste; however quartz sand replacement for 20 % cement does not change the dilatancy of the paste (Fig. 9).

Fig. 11 illustrates the dependence of dilatancy rates D and D_1 on different amounts of plasticizing admixtures in the cement paste (W/C = 0.55) with the same amount of quartz sand. The curves in the figure show that with the increase of the amount of plasticizing admixtures from 0.2 %to 1.0 % and with the same amount of quartz sand (10 %), dilatancy rates D and D_1 are the highest when PP

superplasticizer is used, and the lowest in cement pastes with SNF superplasticizer and L plasticizer.

a

b

Fig. 10. Dependence of dilatancy rates D (a) and D_1 (b) on the amount of finely ground quartz in Portland cement paste: 1 – with L plasticizer; 2 – with SNF superplasticizer; 3 – with PP superplasticizer

The influence of chemical admixtures (plasticizers and superplasticizers) on dilatancy of cement paste was investigated in the previous research work [21, 22, 25]. It was determined that plasticizing admixtures, irrespective of their chemical composition, reduce the yield stress and viscosity of cement pastes, but also increase the dilatancy of the pastes. SiO_2 micro particle suspension combined with plasticizing admixtures changes the dilatancy of the cement paste in a different manner: silica fume combined with superplasticizer based on polycarboxylic polymer increases the dilatancy, while silica fume combined with superplasticizer based on naphthalene formaldehyde resins and plasticizer based on lignosulphonates reduces the dilatancy of cement pastes. Finely ground quartz sand differently to the silica fume suspension increases dilatancy of cement paste with different type of chemical admixtures. Finely ground quartz sand is unsuitable like additive for dilatancy of cement paste reduction.

Dilatancy is higher in cement pastes with quartz sand and higher plasticizing admixture content compared to the pastes with quartz sand and lower chemical admixture content, except for the paste with L plasticizer, the shear

a

b
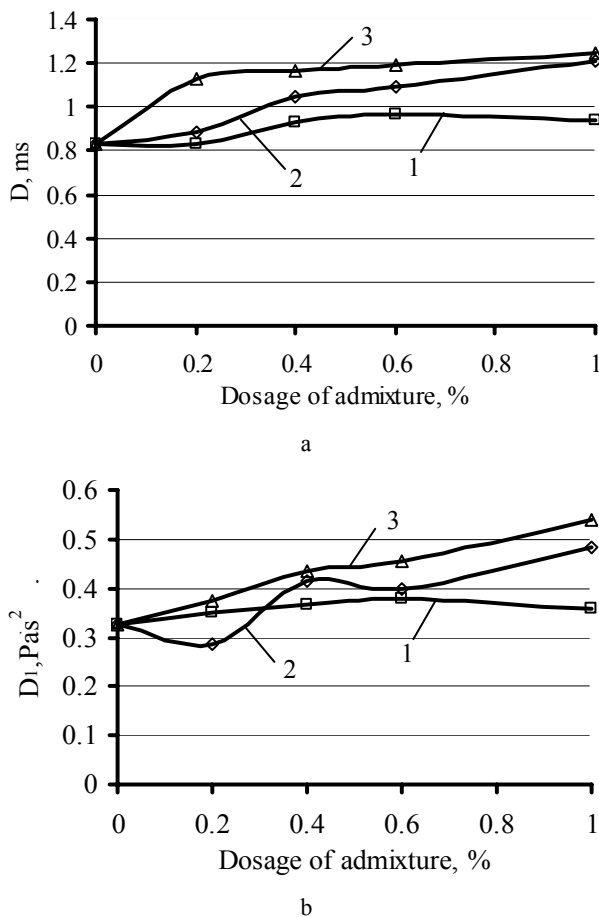
Fig. 11. Dependence of dilatancy rates D (a) and D_1 (b) on different amounts of plasticizing admixtures in Portland cement paste: 1 – with L plasticizer; 2 – with SNF superplasticizer; 3 – with PP superplasticizer

thickening behaviour of which does not change when this admixture replaces from 0.2 % to 1.0 % cement.

4. CONCLUSIONS

1. Finely ground quartz replacing up to 5 % cement without plasticizing admixtures insignificantly reduces the yield stress and viscosity of the cement paste, whereas bigger amounts of this additive does not have a further effect on the rheological properties of the paste.

2. Yield stress and viscosity of the cement paste with finely ground quartz additive and plasticizing admixtures decrease with higher content of plasticizing admixture in the paste irrespective of the chemical composition of the plasticizing admixture.

3. Finely ground quartz with particle size similar to the size of cement particles increases the dilatancy of the paste. The biggest effect on the pastes dilatancy is observed when 5 % of the cement is replaced with ground quartz. The shape and fineness of the ground quartz particles are important for the pastes dilatancy.

4. Finely ground quartz sand (replacing 5 % ÷ 20 % of cement) used in combination with plasticizing admixtures increases the dilatancy of the cement paste irrespective of the chemical composition of the admixture.

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