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Complex Influence of Plasticizing Admixtures and Sodium Silicate Solution on Rheological Properties of Portland Cement Paste

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Complex influence of sodium silicate solution (NSS) and plasticizing admixtures, comprising polycarboxylic polymers, on yield stresses, viscosity and dilantancy of the cement paste has been determined experimentaly. It was determined that the yield stresses in cement paste with superplasticizer comprising polycarboxylic ethers and sodium silicate solution reduce when NSS is added up to 0.8 % by weight of the cement, yield stresses increase abruptly when NSS content in the paste is from 0.8 % to 1 %, and remain constant when NSS content is increased up to 2.0 % by weight of the cement. Yield stresses in cement paste with superplasticizer comprising polycarboxylic polymers, modified by naphthalene formaldehyde resin, and NSS, increase gradually by raising NSS content up to 2.0 % by weight of the cement. Dilatancy of cement paste with superplasticizer comprising polycarboxylic ethers reduces when NSS is added up to 0.2 % by weight of the cement; with further increase of NSS content up to 1.2 % by weight of the cement the dilatancy remains constant and when that amount is exceeded the slurry becomes pseudoplastic. Negative dilatancy factor in slurries with superplasticizer comprising polycarboxylic polymers, modified by naphthalene formaldehyde resin, and 0.5 % NSS indicates pseudoplastic state of the paste, which shifts into the state of similar dilatant slurry without NSS. Performed tests have proven that the tested nanomodifier is a good regulator of rheology of the slurry made of Portland cement and polycarboxylic superplasticizer.

Keywords: Portland cement, sodium silicate solution (NSS), plasticizing admixture, cement slurry, rheology.

1. INTRODUCTION

Cement pastes are classified as structural systems that have certain rheological properties. By the form of structural system rheological curve [1, 2] several groups of structural fluids are distinguished: Newtonian fluids, pseudo-plastic fluids, dilatant fluids, Bingham bodies, plastic dilatant bodies and pseudo-plastic bodies. Cement pastes and concrete slurries are often classified as Bingham bodies (systems) that have two basic rheological characteristics – yield stresses τ_0 and structural viscosity η [3 – 5].

Various chemical admixtures are used in practise to adjust rheological properties of cement slurries and concrete mixtures. Plasticizers and superplasticizers that alter rheological properties of concrete mixtures are used as plasticizing admixtures [6, 7]. The efficiency of plasticizing admixtures depends on their chemical composition [8, 9]. Rheological properties of concrete mixtures are also changed by air-entraining admixtures that increase frost resistance of concrete. Stabilizing admixtures are also used to reduce segregation of concrete mixtures and bleeding and have influence on the mixtures thixotropy [10, 11]. These admixtures are used to improve transportation of concrete mixtures by pumps.

Sodium silicate solution admixture, like plasticizing admixtures, contains nano structures, and sodium silicate solution contains undissolved SiO_2 nanoparticles whose size reaches 1 nm – 2 nm [12 – 4]. These particles induce additional intra-atomic bonding, increase the viscosity of liquid phase that assist the connection of cement and aggregate grains, increase resistance to segregation and improve flowability of the cement slurry [15]. To obtain better characteristics of construction materials at macro level, deliberate adjustment of the formation of these phases must be attempted and properties of these materials at micro level should be researched because nanoadmixtures in cementitious materials act as additional crystallization centres, which change the direction and rate of physical and chemical processes [16]. H. Hommer, K. Wutz and H. Li claim in their studies that new generation superplasticizers not only disperse the material but also act actively on cement hydration process; admixtures containing nanodispersive particles improve the nanostructure of cementitious materials [17, 18].

Previous research has shown that Bingham model gives imprecise description of cement paste flow curves. The flow curves of these pastes are not straight lines as in Bingham model; higher shear stress turns them into curves [19 – 21]. That proves that cement pastes are dilatant structures, i. e. higher shear stress increases the system's viscosity. However the ratio that could be used to evaluate the dilatancy of pastes and slurries is not available. Reynolds claimed that viscosity increases due to increased volume of dispersive system caused by the changes in volumetric dislocation of phase particles, as the particles change their position in relation to each other, and relatively decreased volume fraction of the dispersed phase [22].

According to C. Hu and F. de Larrard the phenomenon of dilatancy is related to the examined material and test methods. They have determined that there is no interrelation between dilatancy and Bingham's rheological characteristics namely yield stresses and structural viscosity [4].

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F. Kaplan, J. Pivinskij and A. Saprykin [23] researched rheological properties and dilatancy of concentrated hydrodispersive quartz glass and detected a correlation between dilatancy and electrical conductivity and electrokinetic (zeta) potential with the change of medium pH from 2 down to 9. Rheological properties of dispersive systems were determined by means of rotating viscometer with coaxial cylinders within rate gradient shift limits of $0.7\ \mathrm{s}^{-1} - 700\ \mathrm{s}^{-1}$. The authors described the initial dilatant flow of concentrated dispersive system by the following equation:

$$\tau = \eta \cdot \overline{\gamma}^{n}, \tag{1}$$

here: τ – is the shear stresses (Pa), γ – is the shear rate (s^{-1}), η – is the viscosity (Pa·s), n – is the degree of dilatancy ($n > 1$).

At all pH values the degree of dilatancy n was close to 1.2 and only the viscosity ratio η changed. The authors propose to evaluate the dilatancy of concentrated dispersive systems at high rate gradients according to the following equation:

$$\tau = \tau_0 \exp(\Gamma \overline{\gamma}), \tag{2}$$

here: τ_0 – is the yield stresses (Pa), Γ – is the time (ms) used to evaluate the system's dilatancy, $\overline{\gamma}$ – is the shear rate (s^{-1}).

The diagram of this function in logaritmic coordinates ($\lg\tau$ versus $\overline{\gamma}$) is the straight line whose slope angle is characterized by the time ratio Γ. This ratio, calculated by the method of least squares, increases from 17 ms (at pH = 2.1) to 132 ms (at pH = 9). From this equation we can also compute the critical rate gradient $\overline{\gamma}_{cr}$ corresponding to the initial intensive dilatant stiffening of the dispersive system; it shows the beginning of the straight line-part in the curve. In this case $\overline{\gamma}_{cr}$ can describe the dilatancy of the system. As electrical charge of the particles increases, $\overline{\gamma}_{cr}$ goes down from $70\ \mathrm{s}^{-1}\,\mathrm{A}$ to $6\ \mathrm{s}^{-1}\mathrm{A} - 8\ \mathrm{s}^{-1}\mathrm{A}$.

J. Efremov [24] claims that the intensity of dilatant stiffening of concentrated dispersive systems depends on the size, form and concentration of solid phase particles, composition and viscosity of dispersion medium, presence of adsorptive and ionic layers, coagulation stability of the system and other factors. The author also states that the absence of adequate theoretical models, shortage of data on the influence of different factors on the dilatancy of concentrated dispersed systems prove the obscurity of this phenomenon.

Based on Reynolds theory J. Goddard uses the phenomenon of dilatancy to explain the plastic properties of granular materials. According to the author, the dilatancy of dispersive systems depends on the friction between solid phase particles and volumetric distribution of these particles [25].

The purpose of the research is to examine the complex influence of plasticizing admixtures comprising polycarboxylic acid-based polymers and sodium silicate solution, used as nanomodifier, on rheological properties of cement pastes: yield stresses, viscosity and dilatancy.

2. MATERIALS AND METHODOLOGY

JSC "Akmenės cementas" Portland cement CEM I 42.5 R was used for the test. Water demand for normal consistency Portland cement slurry is 25.4 %, specific surface area is 360 m^2/kg, particle density is 3110 kg/m^3, and dry bulk density is 1220 kg/m^3.

Two types of plasticizing admixtures were used in the tests, namely superplasticizer F (produced by MC-Bauchemie Miuler GmbH and Co, Germany) and superplasticizer R (produced by Remei GmbH and Co, Germany). Superplasticizer F, comprising polycarboxylic ethers, is a liquid of the colour ranging from light yellow to reddish brown and containing 36.1 % of dry matter; density of the solution is 1.06 kg/l, pH is 4.4 and electrical conductivity is 1.48 mS/cm. Superplasticizer R, comprising polycarboxylic polymers, is a brown liquid containing 18.7 % of dry matter; density of the solution is 1.05 kg/l.

Liquid glass $\mathrm{Na_2O{\cdot}nSiO_2}$ water solution (made by Lithuanian's company Remesta) (NSS) was also used in the tests as nanomodifier of rheological properties of the pastes. NSS is a yellow or light brown solution with the silicate module 3.3, dry $\mathrm{Na_2O{\cdot}nSiO_2}$ and water ratio 60 : 40; the average density value is 1.382 kg/l, liquid glass solution pH is 11.28, and electrical conductivity is 30 mS/cm.

pH and electrical conductivity of the solutions were determined by using a Mettler-Toledo device MPC 227 (pH electrode InLab 410, measuring accuracy 0.01 pH; electrical electrode InLab 730, measuring interval (0 – 1000) µS/cm). The measuring was performed at ambient air temperature 21 °C ±0.5 °C.

Dynamic viscosity of the solutions and cement pastes were tested by Malvern Instruments vibroviscometer SV-10, the principle of whose operation is based on electromagnetic force driven vibration of two acoustic plates in a 13 ml container. Viscosity measuring interval is 0.3 mPa·s – 10000 mPa·s.

Cement pastes were mixed by automatic forced mixer Automix in accordance with LST EN 196-1 standard. The cement (c) was dosed by mass while water (w) and chemical admixture were dosed by volume. Constant w/c ratio of 0.27 was maintained throughout the tests. Liquid plasticizing admixture was mixed into water used for the cement paste. Superplasticizer F was added to the cement paste at 0.5 % by weight of the cement and superplasticizer R was added at 0.75 % by weight of the cement. Sodium silicate solution was added at 0.2 % –2.0 % by weight of the cement; this solution was also mixed into water used to prepare the cement paste.

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 another article [26].

3. RESULTS AND DISCUSSIONS

Flow curves of the cement paste (w/c = 0.27), with superplasticizer F added at 0.5 % by weight of the cement and sodium silicate solution added at 0 % – 2.0 % by weight of the cement are shown in Fig. 1, and the flow curves with the superplasticizer R added at 0.75 % by weight of the cement and sodium silicate solution (NSS) added at 0 % – 2.0 % by weight of the cement are shown in Fig. 2.

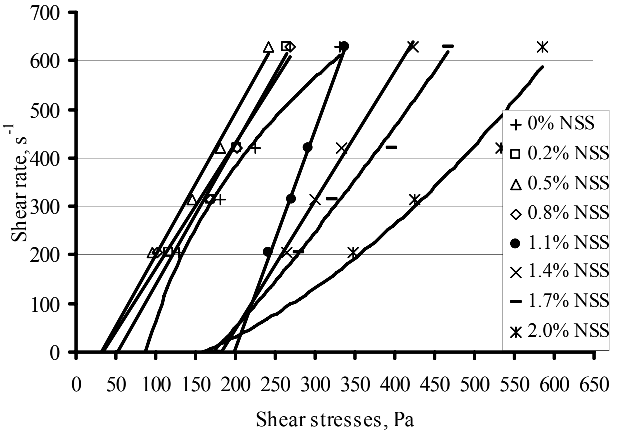

Fig. 1. Shear rate dependence on shear stresses of Portland cement paste with superplasticizer F and NSS

The slope angles of flow curves in this picture show that NSS reduces the dilatancy of cement paste with superplasticizer F at 0.5 wt% of the cement. When NSS is added at 0.2 wt% to 1.4 wt% of the cement the flow curves correspond to linear Bingham model [1, 2] compared to the cement paste without NSS, the flow curve of which is specific to dilatant structures. When NSS content is further increased from 1.7 wt% to 2.0 wt% of the cement, the flow curve corresponds to the flow curve of pseudoplastic bodies.

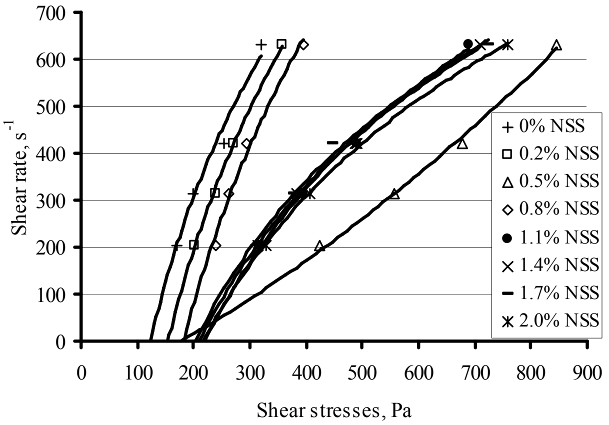

Fig. 2. Shear rate and shear stress functions of Portland cement paste with superplasticizer R and NSS

Fig. 2 shows that dilatancy is characteristic of cement pastes with superplasticizer R (0.75 wt%) and NSS at 0.2 wt% – 2.0 wt% of the cement, except for 0.5 wt% of the cement. The flow curves of these pastes are not linear and do not correspond to Bingham model, but are curved instead. This may be seen by the angles of flow curve slopes – they are inclined towards the axis of shear stresses. The bigger inclination of the slope curve towards the shear stress axis, the higher is the dilatancy of the cement paste. However, with NSS content at 0.5 % by weight of the cement the flow curve of the cement paste with superplasticizer R (0.75 wt%) becomes the flow curve of a pseudoplastic body. The type of this flow curve resembles the curve of the cement paste with superplasticizer F, when NSS is added at 1.7 % – 2.0 % by weight of the cement.

Dependence of yield stresses of Portland cement paste (w/c = 0.27) with superplasticizer F at 0.5 wt% of the cement and superplasticizer R at 0.75 wt% of the cement on the content of NSS wt% is shown in Fig. 3. Yield stress is the point where the flow curve crosses the shear stress axis (Fig. 1 and Fig. 2).

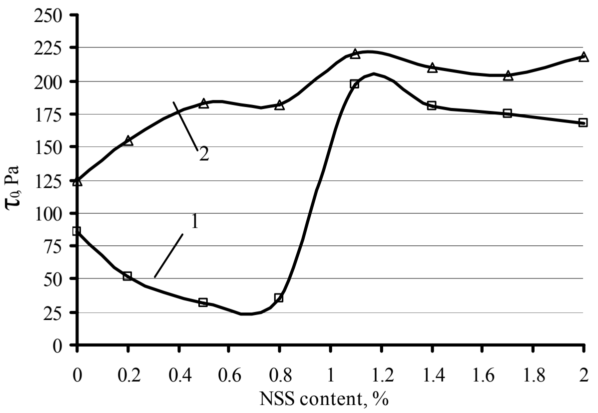

Fig. 3. Dependence of Portland cement paste yield stresses on NSS content: 1 – with superplasticizer F; 2 – with superplasticizer R

The curves in this figure demonstrate that yield stresses of the cement paste (w/c = 0.27) with superplasticizer F (at 0.5 % by weight of the cement) go down when NSS is added up to 0.8 % by weight of the cement. Further increase of NSS up to 2.0 % by weight of the cement result in significant increase of yield stresses of the paste – up to 4.5 times. With NSS added at 1.2 % by weight of the cement the highest yield stresses of the paste are observed. Yield stresses of the cement paste with superplasticizer R (0.75 % by weight of the cement) go up with adding NSS from 0.2 % to 2.0 % by weight of the cement. When NSS is added at 1.1 % by weight of the cement the highest yield stresses of the paste are observed too. The comparison of the effect of both superplasticizers on yield stresses of cement pastes with sodium silicate solution have revealed that superplasticizer F, comprising polycarboxylic ethers, produces a higher plasticizing effect (reduces yield stresses of the paste when NSS is added at 0.8 % by weight of the cement) than superplasticizer R comprising modified polycarboxylic polymers. This difference may result from higher concentration of superplasticizer F (36.1 % of dry matter) compared to superplasticizer R (18.7 % of dry matter); however the content of the latter chemical admixture was by 0.25% higher compared to superplasticizer F content.

The dependence of Portland cement paste (w/c = 0.27) with superplasticizer F viscosity on NSS content at shear-rate being 205 s^{-1} and 630 s^{-1} are shown in Fig. 3, and the dependence Portland cement paste with superplasticizer R viscosity on NSS content at shear-rate being 205 s^{-1} and 630 s^{-1} is shown in Fig. 4.

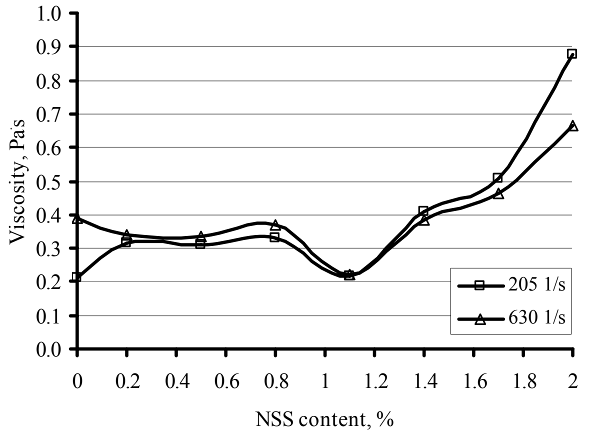

Fig. 4. Dependence of Portland cement paste with superplasticizer F viscosity on NSS content at shear rate 205 s^{-1} and 630 s^{-1}

Curves in Fig. 4 demonstrate that viscosity of the cement paste with superplasticizer F added at 0.5 % by weight of the cement increases when NSS content is increased from 0.2 % to 2.0 % by weight of the cement at shear rate 205 s^{-1} and 630 s^{-1}. When NSS is added at 1.1 % by weight of the cement the lowest Portland cement paste viscosity is observed. The increase in cement paste viscosity is observed with addition of NSS starting from 1.4 % by weight of the cement.

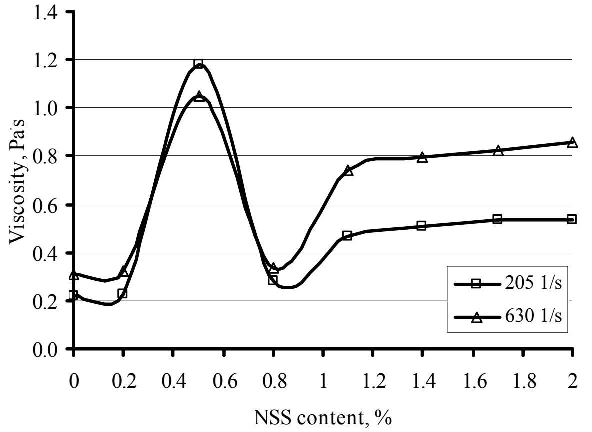

Fig. 5. Dependence of Portland cement paste with superplasticizer R viscosity on NSS content at shear rate 205 s^{-1} and 630 s^{-1}

Viscosity of the Portland cement paste with superplasticizer R increases with the increase of NSS content from 0.2 % to 2.0 % by weight of the cement (Fig. 5). Immediate increase in viscosity has been noticed when NSS was added at 0.5 % by weight of the cement. The same increase in Portland cement paste viscosity was observed in repeated testing. The thickness of the cement paste observed with addition of NSS at 0.5 % by weight of the cement may result from different physical and chemical processes.

According to some authors [16] the shift of dispersion system from sol to gel may be one of such processes. Gel is a specific, semi-liquid, semi-solid, compact, non-flowing thick mass formed when colloidal particles contact the molecules of the dispersion medium. Sol is a colloidal dispersion system or colloidal solution with dispersed phase particles of 1 nm – 100 nm in dimension. Sodium silicate solution contains undissolved SiO_2 nanoparticles of the size up to 1 nm – 2 nm [12 – 14]. H. Hommer, K. Wutz and H. Li claim in their studies that new generation superplasticizers comprise nanodisperse particles [17, 18]. Therefore these solutions may be classified as colloidal solutions or sols. Such colloidal solutions tend to coagulate or turn into gel, i. e. colloidal solution particles flocculate and form bigger aggregates. These bigger aggregates settle down slowly. Coagulation starts with the drop in charge of colloidal particles and becomes very fast when the charge becomes neutral. To induce coagulation of colloidal particles electrolytes are used, sol of opposite charge is added to a colloidal solution, its temperature is raised or electrophoresis is applied. Many hydrophilic colloids coagulate in the presence of electrolytes because hydrating electrolyte ions attract much water, even the water related to dispersed phase particles [28].

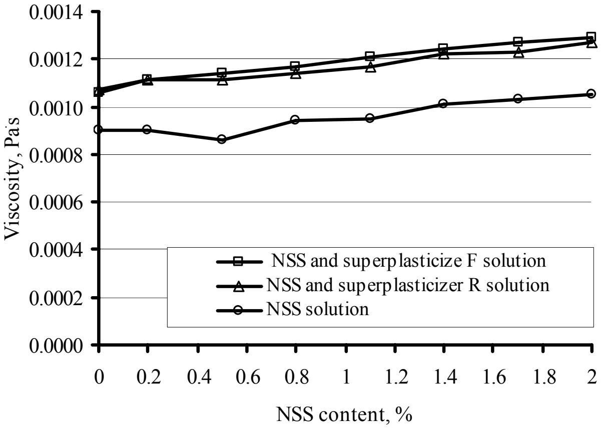

Fig. 6. Dependence of water dispersion viscosity on NSS % in the dispersion

When acidic component, i. e. superplasticizer F (with solution pH of 4.4, electrical conductivity of 1.48 mS/cm) and alkaline component, i. e. sodium silicate admixture (with solution pH of 11.28, electrical conductivity of 30 mS/cm) are mixed at the proportion 1 : 1, such a colloidal dispersion system coagulates and becomes a gel with yellowish brown sediments. The newly formed coagulation system solution has pH of 10.5 and electrical conductivity of 14.5 mS/cm at ambient air temperature of 21 °C ±0.5 °C. Fig. 6 shows the dependence of the viscosity of NSS admixture with superplasticizer F water dispersion (270 ml of water; 5 ml of superplasticizer F; 0 ml ÷ 20 ml of NSS), NSS admixture with superplasticizer R water dispersion (270 ml of water; 7.5 ml of superplasticizer R; 0 ml ÷ 20 ml of NSS) and NSS admixture water dispersion (270 ml of water; 0 ml ÷ 20 ml of NSS) on NSS content % in the dispersion. The curves in Fig. 6 demonstrate that NST dispersion viscosity grows with the increase of NSS content in water dispersion from 0.2 % to 2.0 %; however the viscosity of such dispersion is lower compared to the viscosity of dispersion with NSS and superplasticizer. When one of plasticizing admixtures is added to NSS water dispersion the increased viscosity may indicate the start of coagulation in the system or colloidal sol turning into gel.

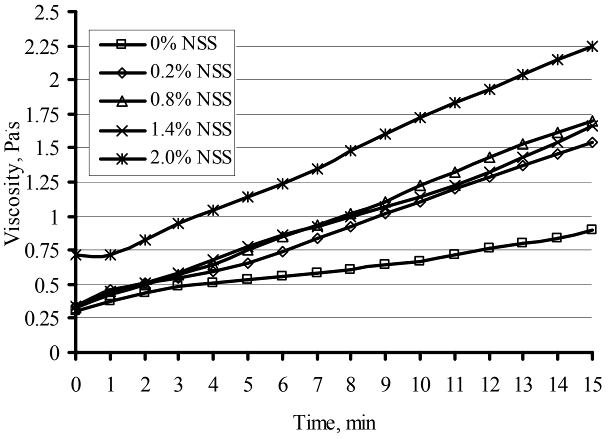

Fig. 7. Time dependence of viscosity of Portland cement paste with superplasticizer F with the increase of NSS % by weight of the cement

Fig. 7 shows the dependence of Portland cement paste (w/c = 0.27) with superplasticizer F (0.5 wt%) viscosity on time when NSS content is increased from 0.2 % to 2.0 % by weight of the cement. As seen from this figure, with the increase of NSS content % by weight of the cement, Portland cement paste viscosity increases with increased time duration. However, The viscosity of Portland cement paste with superplasticizer F when NSS admixture is added at 2.0 wt% of the cement is much higher than the viscosity of Portland cement paste with superplasticizer F with the same NSS content. The increase in viscosity of Portland cement paste (w/c = 0.27) with superplasticizer F (0.5 wt%) with higher NSS admixture could be explained by coagulation among colloidal particles in dispersion medium. The observed thickening of Portland cement paste technologically may have a positive effect on the stability of the slurry, reduce segregation and water separation from such system. These things are very important in order to improve good flowability of the concrete mixtures along tubes and pumping systems.

Fig. 8 shows the values of Portland cement paste (w/c = 0.27) dilatancy factor D [26] at different NSS % by weight of the cement. Dilatancy factor D indicates the growth of cement paste viscosity with the change of shear stresses at rate gradients 205 s^{-1} and 630 s^{-1}. This figure shows that sodium silicate solution reduces the dilatancy of Portland cement paste with superplasticizer F (comprising polycarboxylic ethers) when NSS content ranges from 0.2 % to 1.1 % by weight of the cement (Curve 1). When NSS is added at 0 % – 1.1 % by weight of the cement, the dilatancy factor changes from 0.88 ms to 0.04 ms. When NSS content is at 1.4 % – 2.0 % by weight of the cement, dilatancy factor becomes negative and changes from –0.17 ms to –0.90 ms. In this case negative dilatancy factor may reveal the appearance of thixotropy in dispersion system. Thixotropy is an isothermically reverse shift of a structured system into a non-structured or weak structured system under mechanical agitation, i. e. the ability of the system to restore its structure within a period of time after mechanical disturbance. Rheological flow curves have shown earlier that with NST content at 1.7 % – 2.0 % by weight of the cement Portland cement pastes with superplasticizer F (0.5 wt%) demonstrate pseudoplastic flow. With higher shear-rate the effective viscosity continues decreasing as long as there is a possibility for solid particle orientation along the flow direction; afterwards the flow curve becomes a line. NSS has a positive effect in reducing the dilatancy of cement paste with superplasticizer F.

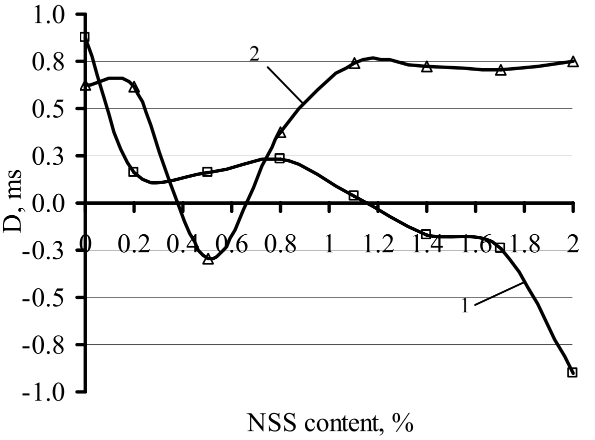

Fig. 8. Dependence of Portland cement paste dilatancy factor on NSS content: 1 – with superplasticizer F; 2 – with superplasticizer R

Dilatancy of Portland cement paste with superplasticizer R (comprising polycarboxylic polymers) when the content of added NSS ranges from 0.2 % to 2.0 % by weight of the cement (Curve 2), except for the drop of dilatancy factor down to 0.30 ms, when NSS is at 0.5 % by weight of the cement. When NSS is added at 0.5 % by weight of the cement to the cement paste with superplasticizer R, such a paste demonstrates pseudoplastic flow (Fig. 2). NSS has a negative effect on reducing dilatancy of the cement paste with superplasticizer R.

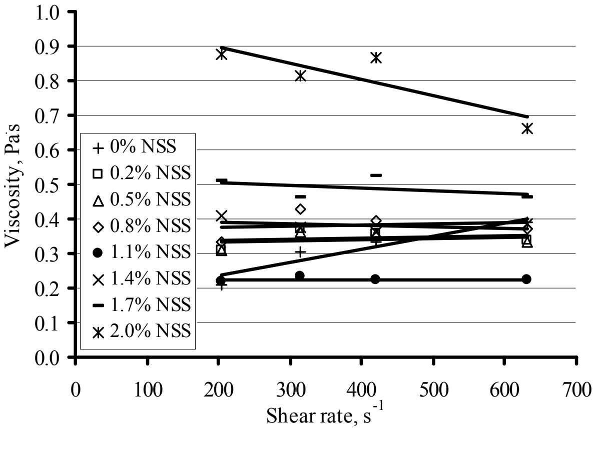

Fig. 9. Share rate dependence of viscosity of Portland cement paste with superplasticizer F and NSS

Dilatancy of the cement paste may be evaluated by another factor D1 according to the slope angle of the curve showing the dependence of viscosity on shear-rate [26]. Dilatancy factor D1 shows how viscosity of the paste or slurry increases with the growth of shear-rate from 205 s^{-1} to 630 s^{-1}. The dependence of viscosity of Portland cement paste (w/c = 0.27) with superplasticizer F (0.5 wt% of the cement) and NSS content at 0 % – 2.0 % by weight of the cement on shear-rate is shown in Fig. 9, and dependence of viscosity of Portland cement paste (w/c = 0.27) with superplasticizer R (0.75 wt% of the cement) and NSS content at 0 % – 2.0 % by weight of the cement on shear rate is shown in Fig. 10.

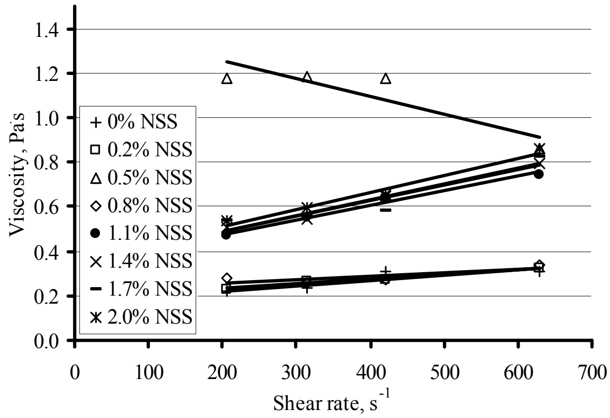

Fig. 10. Share rate dependence of viscosity of Portland cement paste with superplasticizer R and NSS

Lines in Fig. 9 clearly show that when NSS at 0.2 % – 1.4 % by weight of the cement is added to Portland cement paste with superplasticizer F (0.5 wt% of the cement) the viscosity does not change with growing shear-rate. The viscosity of cement paste without NSS increases about 1.8 times with the shear rate growing from 205 s^{-1} to 630 s^{-1}; this shows the occurrence of dilatancy in the paste. The same is confirmed by rheological flow curve (Fig. 1) and aforementioned dilatancy factor D (Fig. 8). Viscosity of Portland cement paste with superplasticizer F and NSS at 1.7 % and 2.0 % by weight of the cement reduces about 1.1 and 1.3 times respectively (Fig. 9). When NSS is added at 0.2 % – 2.0 % by weight of the cement viscosity of Portland cement paste with superplasticizer R (0.75 wt%) increases with the growth of shear-rate, except for the case when NSS content is 0.5 % by weight of the cement (Fig. 10). Then the viscosity of cement paste drops by 1.1 times. Viscosity of cement paste without NSS increases about 1.4 times as the shear rate grows from 205 s^{-1} to 630 s^{-1}. The same is confirmed by rheological flow curve (Fig. 2) and aforementioned dilatancy factor D (Fig. 8). This shows that NSS admixture reduces cement paste dilatancy.

CONCLUSIONS

1. Yield stresses in cement paste with superplasticizer comprising polycarboxylic ethers and Sodium Silicate solution reduce when NSS is added up to 0.8 % by weight of the cement; when NSS is added at 1.2 % by weight of the cement, yield stresses increase abruptly and remain constant with further addition of NSS up to 1.2 % by weight of the cement. Yield stresses in cement paste with superplasticizer comprising polycarboxylic polymers, modified by naphthalene formaldehyde resin, and NSS, increase gradually by raising NSS content up to 2.0 % by weight of the cement.
2. Viscosity of cement paste with superplasticizer comprising polycarboxylic ethers and Sodium Silicate solution slightly reduces when NSS is added up to 1.2 % by weight of the cement and increases when this amount is exceeded. Viscosity of cement paste with superplasticizer comprising polycarboxylic polymers, modified by naphthalene formaldehyde resin, and NSS increases when NSS content is raised from 0.2 % to 2.0 % by weight of the cement, except for extreme viscosity when NSS is added at 0.5 % by weight of the cement.
3. Sodium Silicate solution reduces dilatancy of slurries with superplasticizer comprising polycarboxylic ethers when NSS is added up to 0.2 % by weight of the cement; with further increase of NSS content up to 1.2 % by weight of the cement the dilatancy remains constant and when that amount is exceeded the slurry becomes pseudoplastic. Negative dilatancy factor in slurries with superplasticizer comprising polycarboxylic polymers, modified by naphthalene formaldehyde resin, and NSS indicates pseudoplastic state of the paste.

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