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Determination of Dispersion Efficiency of Cement Suspensions by Method of Centrifugation

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ABSTRACT: In this research, rheological parameters of cement suspensions modified with different doses of two types of superplasticizers (SPs) were evaluated with an alternative method of centrifugation. It was determined that the critical normal and shear stresses (yield values), and the water/solid ratio alter with the additive dose, the additive type as well and the magnitude of centrifugal forces. The results obtained reveal that the method of centrifugation might serve for determination of dispersing effectiveness of SPs and rheological parameters of suspensions in general. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 464–471, 2013

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INTRODUCTION

The accuracy and reproducibility of rheological measurements of cement suspensions depend on a number of variables (water/cement ratio, type of additives or parameters of cement and mixing process).[1–7] However, the results may be influenced by the segregation of phases if the water/cement ratio is high, or conversely, plastic flow in the shear gap might not be sufficient or interrupted if this ratio is low, when traditional coaxial-cylinder rheometer is used. Further, if cone-plate or plate-plate rheometers are used, the formation of a water-rich gliding layer could lead to measurement errors. Therefore, various surface (profilation) treatments of the cone or plate and modified inert rotating cylinders have been tested.[8,9] In this way, the rheological regimes used are the cone method, shear stress ramp, slump test (which is widely used for cement mortars), and the oscillation method.[10,11] Except of the last mentioned the shearing tests cause destruction of formed structure. In this respect, the consolidation/concentration of suspended particles under exposure of an external force such as gravity or pressure differential provides data on the degree of separation of particulate suspensions.[12–14]

It has been reported that the strength of inter-particle forces in a network suspension structure (compressive yield stress), suspension state, elasticity, dewaterability, and packing density, which strongly depends on the particle size distribution and the particle size, are key parameters to achieve optimum rheological properties.[15,16] Channell and Zukoski[13] performed and linked together shear and compressive rheological experiments when studying weakly aggregated alumina suspensions. They stated that aggregates or discrete particles can control rheological properties by fixing particle fraction and increasing strength of attraction. An incorporation of the gel transition was necessary to completely describe rheological properties of aggregated suspensions since the gel transition requires the regulation of the attraction strength to the appropriate level.

Leong[17] investigated on ZrO_2 suspensions the relationship between yield stress and inter-particle forces of attraction, long-range attraction, linking and repulsion obtained from surface chemistry controls (pH, ionic strength, and adsorbing additives such as polyacrilic acids, surfactants, sodium dodecyl sulfate, and dodecylamine). In addition, Kjeldsen[18] described that the governing inter-particle forces in cement and concrete are van der Waals force (attractive), electrostatic double-layer force, and polymer-induced steric force (repulsive).

The inter-particle energy for flocculated systems can be controlled by various means. One alternative is adsorbing surfactants with similar dielectric properties as solvent onto solid particles and dispersing powders in a nonaqueous medium.[19,20] As an example, fatty acids of various molecular weights were successfully adsorbed onto alumina suspensions in decalin, providing a short-range steric repulsive interaction that could counteract the ever-present van der Waals forces.[21] Other surfactants that have been used are alkyl alcohols grafted onto Si_3N_4 solid particles,[20] and polyacrylic acid ammonium salts within Si_3N_4.[22]

Using compressive rheology, Garrido and Aglietti[23] achieved improvement of the rheological properties of aqueous suspensions (48 vol %) of alumina-zircon mixtures and polyacrylate-based dispersant by controlling the degree of dispersion. Further work was developed by Tsetsekou et al.,[24] who stabilized slurries of high-solid content for the production of slip-cast objects through the addition of aqueous solution of commercial dispersants (carbonic acid-based, alkali-free polyelectrolyte, and ammonium salts of polymethacrylic acid and acrylic polymer).

The relation of the molecular structure of comb-type superplasticizers (SPs) for the analysis of centrifugal consolidated MgO suspensions was proposed by Bergström et al.,[25] and Kjeldsen et al.,[26] to overcome the problems of sedimentation and poor sensitivity (common problems in steady-shear measurement). However, to our best knowledge no attention has been paid to the influence of centrifugal forces on the efficiency of SPs in cement suspensions.

In general, two main parameters are used to quantify the effects of SP on the cement suspensions: apparent yield stress and viscosity.[27] A number of studies have been reported with concern on the effect of the SPs type and dosage on the rheological properties.[28–31] Adding SP shifts pronouncedly shear thickening towards higher shear rates.[29,32] These rates can be attained in rheometers and may allow for characterizing an impact of admixtures.[32] Chandra and Björnström[33,34] compared the influence of lignosulfonic acid, melamine sulfonic acid, and carboxylic acid-based SPs on the fluidity of mortars. In the study, the fluidity was characterized using the spread of a cone, without detailed rheological investigation. It was found that rheological effectiveness of SPs decreases in order: carboxylic acid > naphthalene sulfonic acid > melamine sulfonic acid. Nevertheless, the results revealed that fluidity changes with time of measurements, and another type of analysis is necessary for determination of SPs efficiency.

Golaszewski and Szwabowski[35] considered similar but more general behavior using rotational rheometer. Rheological parameters of SPs tested show similar effectiveness in high water to cement ratios. The high effectiveness of the carboxylic-based SP was fully revealed only at low-water/cement ratios.

Papo and Piani[36] used both steady and oscillatory shear flows for the investigation of the influence of melamine resin, modified lignosulfonate and modified polyacrilic resin-based SPs on the rheological properties of cement pastes. The study reported similar flow behavior of melamine and lignosulfonate-based SPs, whereas polyacrilic-based SP showed sharp decrease in viscosity corresponding to a critical deflocculant concentration of 0.5 ml/100 g (the optimum dosage). Additional oscillatory tests were necessary to evaluate efficiency of plasticizers more precisely.[36]

Phan et al.,[28] considered transient and steady-state rheological properties of organic additives' modified cement pastes. The rheograms of such pastes were split into three regions: for relatively low-shear rates the pastes behaved as a power-law shear thinning fluid, followed by a "plateau," where the viscosity is independent for shear rate, and shear-thickening at high-shear rates.

Nehdi and Al Martini[37] tested polycarboxylate, melamine sulfonate, and naphthalene sulfonate-based SPs in the cement paste using oscillatory shear tests. The objective was to find a methodology based on an oscillatory shear stress test to predict the yield stress of superplasticized cement pastes under various ambient temperatures and mixing times. It was found that the saturation dosages of additives increase in order: polycarboxylate < naphthalene sulfonate < melamine sulfonate-based SP.

The effect of different SPs was investigated using a coaxial rheometer as well. Test results showed that above certain critical dosage the polyacrilic-based SP resulted in shear-thickening response.[38] Plank et al.,[39] studied the influence of hydroxy termination of the poly(ethylene oxide) side chains in poly{carboxylate-g-(ethylene glycol)-ether} type SP on their performance in cement, using a "mini slump test" according to DIN EN 1015. The results suggested that for the preparation of polycarboxylate admixtures, —OH terminated poly(ethylene glycol) methacrylate monomer offers an attractive alternative to —OMe terminated methacrylates.

Polycarboxylate-based polymers constitute a new family of admixtures (so called third generation SPs),[30,31] which have been developed to further enhance water reduction and its retention through more effective steric dispersion mechanism. These comb polymers consist of a negatively charged backbone with carboxylic groups and grafted side chains composed mainly of polyethylene oxide units. The charged backbone adsorbs on the surface of the hydrating cement particles. The nonadsorbing graft chains extend away from the cement surface into the solution (particles are dispersed via steric repulsion mechanism caused by the side chains).[40]

This article comments on the results obtained using an alternative centrifugation method to determine the dispersion efficiency of two types of SPs in cement suspensions.

EXPERIMENTAL

In the research, laboratory prepared cements were mixed with solutions of different doses of two types of SPs. Further, the cement suspensions were rheologically tested by an alternative centrifugation method described below. Size exclusion chromatography (SEC) was used for molar masses determination of SP, regression analysis and the response surface designs were applied in the evaluation of results.

Cement

Two types of laboratory cement were prepared. The mineralogical composition and the basic parameters of clinkers are given in Table I. Each clinker + 5 % of gypsum were ground in a laboratory ball mill. Clinkers were selected in the respect of different C_3A content (see Table I), which forms ettringite during the early hydration, and negatively impacts rheological properties of suspension.

Superplasticizers

Sulfonated melamine-formaldehyde (MF) condensate is an additive in powder form (Melment F10 X, BASF Construction Polymers, Germany), Figure 1(a). Polycarboxylate ether-based

Table I. Basic Parameters of Cements Used

Cement	Mineralogical composition (%)				Specific surface area (m^2/g)		
	C_3S	C_2S	C_3A	C_4AF	Blaine[a]	BET[b]	D_{90}[c] (μm)
Cement S	65.31	8.7	9.1	16.89	0.52	1.8	35
Cement M	70.1	12.6	2.8	14.5	0.5	1.71	36.8

[a] The specific surface area of cement is determined directly from air permeability. [b] The specific surface area of cement is calculated from physical adsorption of gas molecules, it includes internal surfaces present in microcracks or in pores open at only one end leading to higher results than Blaine. [c] The size of the particle for which 90% of the sample by mass is below this size, measured using laser diffraction techniques.[41]

plasticizer (PC) is liquid additive (Gecedral Fluid 10.1, BK Giulini GmbH Ludwigshafen, Germany), Figure 1(b).

Size Exclusion Chromatography (SEC)

Measurement was performed on Waters 2695 Separation Module equipped with a Ultrahydrogel™ guard column from Waters (Eschborn, Germany). This column contains a support based on hydroxylated methacrylate polymer, compatible with aqueous mobile phases over a wide range of pH (2–12) and it is generally used in the analysis of highly polar macromolecules.[42] The polymer concentration was monitored with a differential refractive index detector (RI 2414, Waters, Eschborn, Germany). Aqueous 0.1 N $NaNO_3$ solution adjusted to pH 12 with NaOH was used as an eluent at a flow rate 1.0 mL/min. Plasticizer concentration in the eluent was 10 mg/ml.

Using SEC, it was possible to indentify two main fractions of the dispersants: 55% of fraction with a molecular weight of 350,000 g/mol and 30% of fraction with a molecular weight of 9000 g/mol for MF, 50% of fraction with a molecular weight of 80,000 g/mol, and 50% of fraction with a molecular weight of 14,000 g/mol for PC plasticizer.

Regression Analysis and Response Surface Designs

The computer program Statgraphics v.7 (Statistical Graphics Corporation) was used for results evaluation. The function between dependent [e.g., water/solid (*W/S*) ratio] and independent (e.g., the critical normal stress on the frontal surface σ_x and SP dose) variables using regression analysis was investigated. Accordingly, correlation limits were taken $R^2 < 30\%$ for poor or any correlation, $30\% < R^2 < 60\%$ for medium correlation, and $R^2 > 60\%$ for good correlation between tested variables.

Centrifugation Method

After the action of external (centrifugal) forces, sedimentation of temporarily suspended solid particles (bleeding) starts, and a quasi-equilibrium state sets in after a certain period of storage. Grainy particles come into contact with each other and form a skeleton with gaps filled by an inter-particle solution. Its volume responds to the volume of gaps (inter-particle volume); the remaining amount of water is separated above the surface of the specimen. Accordingly, the proportion of the *W/S* ratio can be calculated using the following relationship:

$$W/S = \frac{m_l - m_d}{m_s} \tag{1}$$

where m_s, m_l is the mass of solid and liquid phases in suspensions before centrifugation (g) and m_d is the mass of separated water (plasticizer solution) after centrifugation (g).

The suspensions for the measurement were prepared in the following way: 13.5 g (ml) of water (or plasticizer solution) and 13.5 g of cement were placed in a glass cell (cement was poured into the water). Cell with the suspension was immersed in an ultrasonic bath for 15 min to secure the interaction of organic molecules with the surface of solid particles, the dispersion of agglomerates of fine particles, and even the distribution of all fractions of grainy particles throughout the suspension. Centrifugation of the cells with suspensions was conducted immediately after homogenization (Centrifugal machine Rotofix 32, Hettich Zentrifugen, diameter of glass cell was 2 cm). Time of centrifugation was 3 min and different rotation speeds were used. After centrifugation, the separated fraction of water was carefully poured into a Petri dish. The weight of the cell with the remaining amount of the specimen and that of the Petri dish with separated solution (containing a small amount of ultra fine particles) were determined. The weight of the separated water and the content of solids in it were calculated from the weights of the Petri dish before and after 25 min of drying at 105°C. Accordingly, the *W/S* ratio was calculated using the relationship (1).

The cells for centrifugation usually have a cylindrical or conical shape. For experiments in this article, cylindrical cells were used.

Cylindrical Cell Theory

A diagram of the action of external forces on the specimen in the cell during centrifugation is shown in Figure 2, where the following parameters can be discerned:

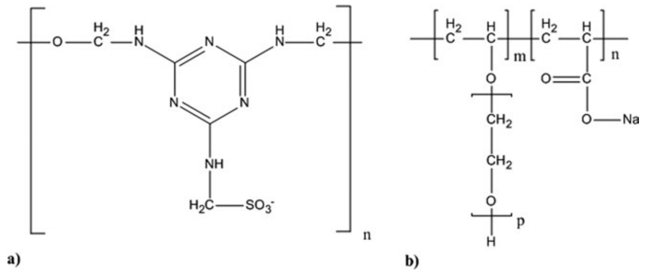

Figure 1. Molecular structure of SP used: sulfonated melamine-formaldehyde condensate (a) and polycarboxylate ether (b).

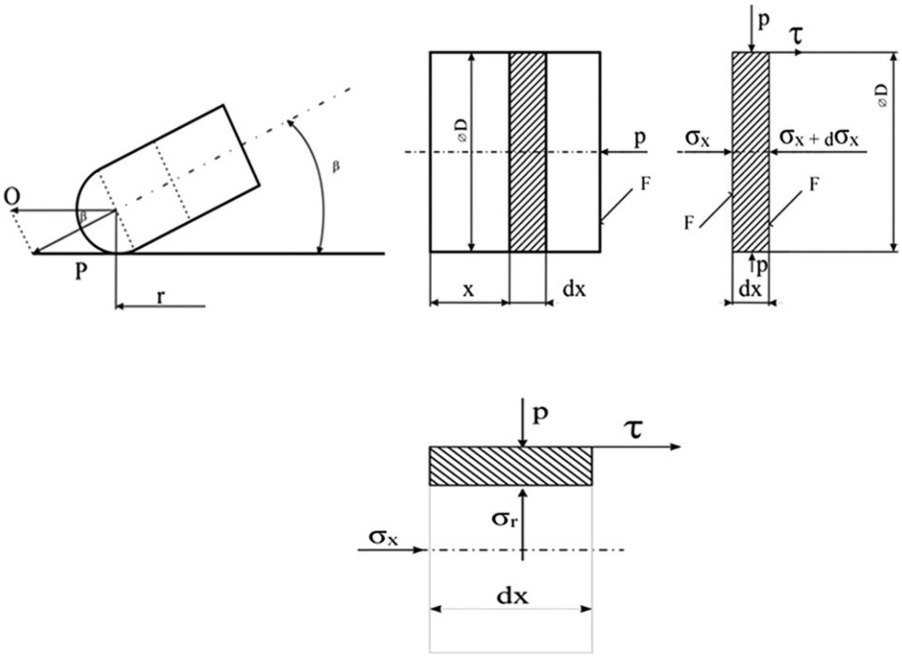

Figure 2. Scheme of cylindrical cell and distribution of forces acting on the specimen during compaction.

O, centrifugal force (N); *P*, compacting force (N); σ_x, normal stress on the frontal surface of element (N/cm^2); *p*, pressure on circumference surface (Pa); τ, shear stress on contact surface (N/cm^2); *F*, cross-section of cell (cm^2); and *D*, diameter of *F* (cm).

The distribution of forces acting on the specimen in the cell depends on its shape and for a cylindrical shape, the force balance in the horizontal direction gives:

$$(\sigma_x + d\sigma_x)F - \sigma_x F - p\pi D dx - \tau\pi D dx = 0 \qquad (2)$$

In addition, the existence of the friction represented by a friction coefficient *f* can be expected in the contact zone:

$$\tau = fp \qquad (3)$$

Consequently, the eq. (2) can be adapted in this way:

$$pdx(1+f) = \frac{D}{4} d\sigma_x \qquad (4)$$

Conversely, the condition for equilibrium of forces acting in a vertical direction on the hatched element (the force balance according to Figure 2) results as follows:

$$\sigma_r dx - pdx + \tau dx = 0 \qquad (5)$$

$$p = \sigma_r + \tau \qquad (6)$$

In the relation (6), σ_r is the radial stress originating due to the compaction of specimen (N/cm^2).

Shear stress can be neglected in comparison with pressure on circumference surface, that is, $\tau << p$, and radial stress is equal to *p*.

Then, under the assumption that specimen deformation characteristics at high circumferential velocity are the same as in the case of plastic materials, the plasticity condition applies:

$$\sigma_1 - \sigma_3 = \sigma_k \qquad (7)$$

where σ_i, stress to *i*-axis (N/cm^2) and σ_k, yield value (N/cm^2).

Equation (7) is valid in the area of 3D state of stress, and the following is also valid:

$$\sigma_1 \geq \sigma_2 \geq \sigma_3 \qquad (8)$$

A structural breakdown occurs, when limiting yield values (critical stresses σ_x and τ) is exceeded and for cylindrical cell criterion plasticity condition is given below:

$$p - \sigma_x = \tau \qquad (9)$$

Having inserted eq. (9) into the relation (4):

$$\frac{d\sigma_x}{\sigma_x + \tau} = \frac{4(1+f)}{D} dx \qquad (10)$$

The mathematic integration of eq. (10) leads to:

$$\sigma_x = \tau\left[e^{\frac{4(1+f)}{D}(x-h)} - 1\right] \qquad (11)$$

In eq. (11), *h* represents the height of specimen in a cell before centrifugation (cm).

At the same time, the following relations were used for calculation of σ_x:

$$P = F\sigma_x \qquad (12)$$

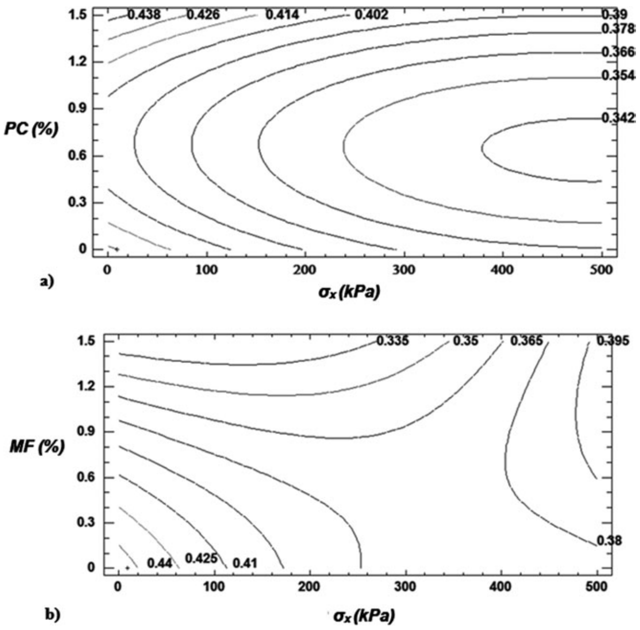

Figure 3. Contour plot for *W/S* ratio as a function of critical normal stress (σ_x) and PC (a) and MF (b) SP dose (each contour line is labeled with a number corresponding to *W/S* value)—cement S.

$$P = O\cos\beta \tag{13}$$

$$O = \frac{G}{g} r\omega^2 \tag{14}$$

$$G = G_0 - V_s\gamma_l \tag{15}$$

where ω, angular velocity (1/s); *G*, mass of solid phase in a suspension (g); G_0, mass of solid phase in a dry form (g); V_s, volume of solid phase (cm^3); γ_l, specific gravity of liquid (g/cm^3); and *r*, centrifuge radius (cm).

According to the assumption that plastic deformation is not distributed during centrifugation, the surface of glass cell is smooth, and there is no formation of slump lines during centrifugation. In this respect, Rebinders relations [eqs. (16) and (17)] were used for calculation of critical shear stress (yield) τ.[43] In this case, the cone was pushed into the mixture after centrifugation and the depth penetration was measured. Especially developed equipment was used for these types of measurements:

$$\tau = \frac{P}{v^2}\cdot K \tag{16}$$

$$K = \frac{1}{\pi}\cos^2\alpha \cot g\alpha \tag{17}$$

where *v*, penetration depth of the cone in the mixture after centrifugation (cm) and α, angle of the penetration depth of the cone in the mixture after centrifugation (°).

RESULTS AND DISCUSSION

Comparison of rheological effectiveness of sulfonated MF and polycarboxylate ether (PC) SPs is discussed to verify the utilization of the centrifugation method in the rheological characterization of cement suspensions. For this part of the investigation, cement M and cement S were used (see Table I). The results are presented through Figures 3–6. Surface response model was used to describe the relationship between the independent variables (the critical normal stress on the frontal surface σ_x and SP dose) and the response variable (*W/S*) for the different types of cements and plasticizers. Experimental data were analysed with the aid of Statgraphics v.7 to obtain a model which describes the effect of σ_x (*A*) and SP dose (*B*) on *W/S*. An example of the model for the parameters depicted in Figure 3(a) is shown below:

$$W/S = 0.43 - 2.43\times10^{-4}A - 9.44\times10^{-2}B + 2.41\times10^{-7}A^2 + 1.32\times10^{-5}AB + 6.91\times10^{-2}B^2 \tag{18}$$

From this model, the partial derivatives were evaluated using the second derivative test for function of two variables, and then set equal to zero to find the critical points. The points found correspond to the minimum dose of PC at which the rheological (deformation) behavior reaches critical (yield) values.

Type of cement and plasticizer influences the response variable (*W/S*) in a different way. The critical normal stress (σ_x) required for reaching the minimum *W/S* value decreases with increasing PC dose. The increment of the stress on the frontal surface affects positively the *W/S* ratio (lower values are obtained) in case of PC SP [Figure 3(a)]. The analysis revealed 0.64% of PC dose (to dry weight of cement) and 486 kPa of σ_x, corresponding to *W/S* value of 0.34, where this SP is the most effective.

The same analysis was applied to reveal the effect of MF additive, Figure 3(b). The course of this dependence is significantly different. As can be seen, lower values of σ_x and higher doses of MF additive have a positive effect on *W/S* value. Minimal *W/S* value (0.34) is achieved when MF dose reaches 1.28% (see Table II).

When cement M was considered to study the efficiency of the two SPs (Figure 4), the same analytical approach was used. As can be seen in Figure 4(a), the effect of PC plasticizer on cement M is rather similar to that acting on cement S—the increment in σ_x decreases the *W/S* ratio to 0.27 in case of 0.84% plasticizer dose. Similarly, the use of cement M with MF provided a lower *W/S* ratio value (0.31) in comparison with cement S (0.34); however, higher value of σ_x (214 kPa) was required.

Overall, the regression analysis showed very good correlation between dependent (*W/S*) and independent (σ_x, plasticizer dose) variables for both types of cement—the correlation

Table 2. Summary of Conditions for the Lowest Water/Solid Ratio Obtained with Different Plasticizers and Critical Stresses

Cement	Type of SP	Concentration (%)	W/S	σ_x (kPa)	τ (N/cm^2)
S	PC	0.64	0.34	486	22
S	MF	1.28	0.34	144	21
M	PC	0.84	0.27	439	26
M	MF	1.28	0.31	214	39

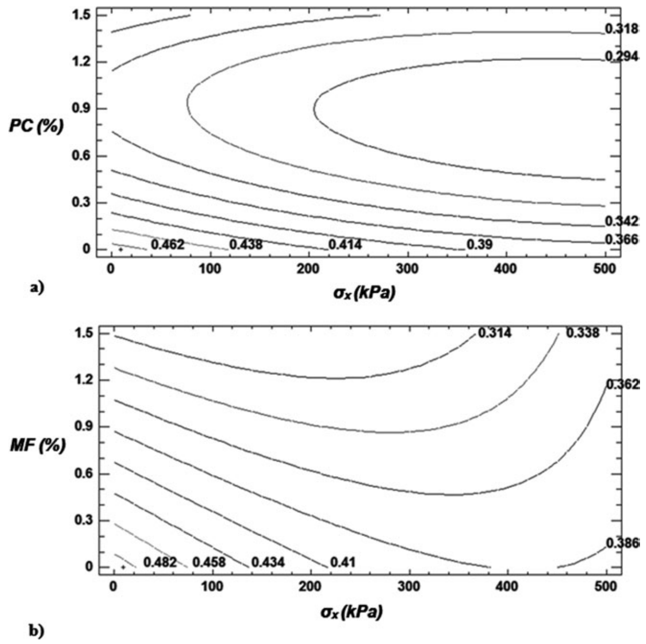

Figure 4. Contour plot for *W/S* ratio as a function of critical normal stress (σ_x) and PC (a) and MF (b) SP dose (each contour line is labeled with a number corresponding to *W/S* value)—cement M.

coefficients R^2 were found to be in the range of 0.90–0.96. From the results summarized in Table II, the performance the PC type of additive is more effective in both cements.

The results of the investigation of the role of PC and MF SPs on the critical shear stress (τ) are presented in Figures 5 and 6. The correlation coefficients of dependent τ and independent (*W/S*, plasticizer dose) variables were in the range from 0.75 to 0.97.

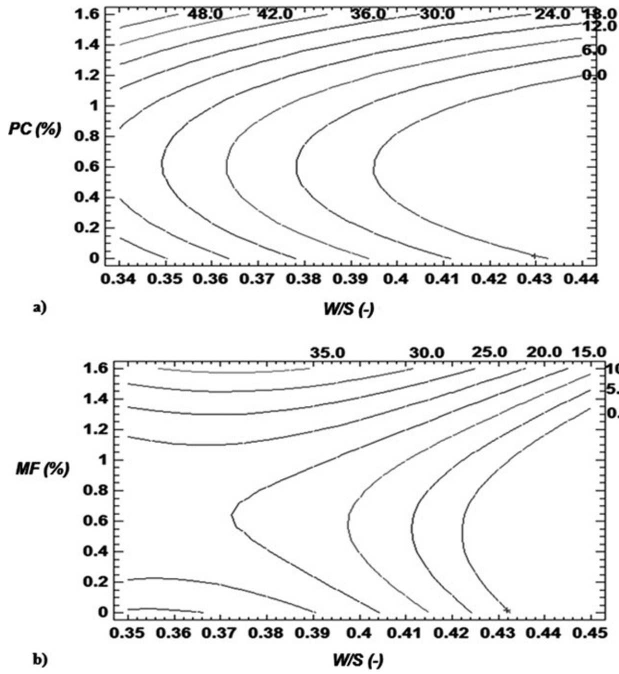

Figure 5. Contour plot for critical shear stress (τ) as a function of *W/S* ratio and PC (a) and MF (b) SP dose (each contour line is labeled with a number corresponding to τ value)—cement S.

The effect of SP on the critical shear stress τ is more pronounced on cement M (26 for PC and 39 for MF), whereas the resulting τ values obtained for cement S are rather similar (22 N/cm^2 and 21 N/cm^2 for PC and MF, respectively). Thus, the use of PC as SP of cement S allows for lower values of the critical shear stress. In addition, at the plasticizer dose of 0.64% PC is the most effective, while a double concentration (1.28%) is needed to obtain equal *W/S* ratio if MF is used (see Table II).

As depicted in Figure 1(b), PC consists of a negatively charged backbone with carboxylic groups and grafted side chains composed of polyethylene oxide units dispersing cement particles by both electrostatic repulsive forces and steric hindrance. It is different mechanism from MF, which enhances fluidity of cement only due to electrostatic repulsion [the structure of polymer without side chains is shown in Figure 1(a)].

It might be noted that apart from the different basic groups of SPs, there can be also variance in the same groups due to SPs synthesis resulting in a different molecular weight and chemical configuration.[33]

Cement suspensions behave as high energy materials and are amphoteric with a predominant basicity. Adding of SP to suspension decreases energy of hydration reactions and deflocculates the cement particles due to adsorbing organic molecules on cement and changing the zeta potential of particle surface to a negative value (particles having the same sign of zeta potential

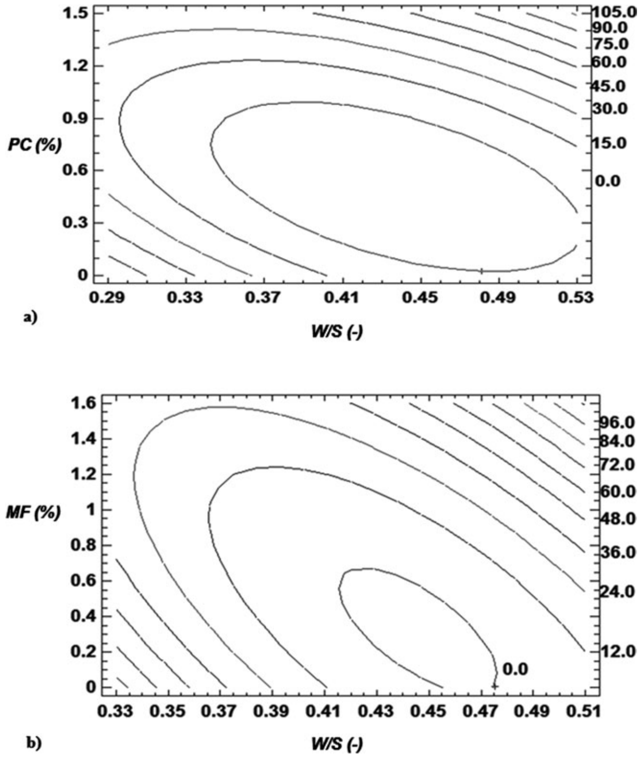

Figure 6. Contour plot for critical shear stress (τ) as a function of *W/S* ratio and PC (a) and MF (b) SP dose (each contour line is labeled with a number corresponding to τ value)—cement M.

cannot approach each other closely due to the electrostatic repulsion).[44] The particles are deflocculated, and the fluidity and processability of suspensions are improved. Following, the properties of concrete are governed by cement suspension flow and thus, addition of SP makes possible preparation of cement paste with lower water/cement ratio and high performance concrete.[33]

In comparison with the viscometer measurements and using insufficient cone-plate method when the suspension viscosity changes markedly with the time of measurements, it was determined that W/S values are stabilized after 3 min of centrifugation and reproducibility of measurements is on the level of 1%. Furthermore, the method is suitable for the study of both high and very low water/cement ratio suspensions (where classical rheometry fails). In comparison to Golaszewski and Szwabowski,[35] high efficiency of carboxylic-based SP is confirmed by centrifugation at high water cement ratio.

CONCLUSION

Dispersion efficiency investigated using a centrifugation method is higher in case of sulfonated polycarboxylate ether-based SP than MF additive. Regression analysis showed very good correlation between dependent and independent variables for both types of cements tested.

The phenomenon investigated—in a certain relation to the equilibrium of external and repulsive forces between charged particles—might originate as a consequence of the sorption of plasticizer molecules on their surfaces. A rapid increase of the plasticizer molecules in the liquid phase of suspension after the maximum sorption on the surface of cement particles could change the proportion of internal and external forces after centrifugation. In this respect, application of centrifugation method (in combination with sorption measurements), in terms of action of external forces in the suspensions leading to an approximation of organic molecules adsorbed on cement particles, might serve as suitable method to investigate action of plasticizers and their dispersion efficiency.

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