Effect of superplasticizers on the rheological properties of cements

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ABSTRACT

In this paper, the rheological properties of cement pastes made with different types of cement and superplasticizers are discussed. As a tool for the discussion, experiments involving dispersion of cement particles, fluidity, viscosity, yield stress and zeta potential have been conducted. The results obtained show that the chemical compositions of the cements such as C_3A and sulfate content, alkali and ground lime content are important features controlling the rheology of cement pastes. Three types of sulfonated superplasticizers (lignosulfonate-based, melamine formaldehyde sulfonic acid, naphthalene formaldehyde sulfonic acid) and one type of polycarboxylic acid polymer were used. The results revealed that the mechanism by which these polymers disperse cement particles differs fundamentally. Sulfonated superplasticizers induced a negative charge on cement particles dispersing them by electrostatic repulsion, whereas with the polycarboxylate-based polymer the dispersion mechanism is mainly controlled by steric hindrance. A model for the adsorption of superplasticizer on a cement particle is proposed.

RÉSUMÉ

Dans ce rapport, les propriétés rhéologiques des pâtes de ciment fabriquées avec différents types de ciment et de superplastifiants sont discutées. Outils de cette discussion, des expériences impliquant la dispersion des particules de ciment, la fluidité, la viscosité, la fonction de ce seuil et le potentiel zêta ont été conduites. Les résultats obtenus montrent que la composition chimique du ciment, comme les teneurs en C_3A et en sulfate, ainsi que les teneurs en alcali et en chaux, sont des particularités importantes afin de contrôler la rhéologie des pâtes de ciment. Trois types de superplastifiants avec sulfate (lignosulfonate, acide sulfonique formaldèhyde mélamine, acide sulfonique formaldèhyde naphthalène) et un type de polymère acide poly-carboxilique ont été utilisés. Les résultats ont révélé que le mécanisme, par lequel ces polymères dispersent les particules de ciment, est fondamentalement différent. Les superplastifiants avec sulfate ont entraîné une charge négative sur les particules de ciment, les dispersant par la répulsion électrostatique, tandis qu'avec le polymère poly-carboxylate, le mécanisme de dispersion est principalement contrôlé par un encombrement stérique. Un modèle pour l'adsorption de superplastifiants par une particule de ciment est proposé.

1. INTRODUCTION

Cement particles have charges on the surface, which make them flocculate in contact with water. In so doing, a part of the water becomes entrapped. This results in less water available for cement hydration. Consequently, it influences upon the consistency of cement paste. Higher water content improves the consistency but decreases the strength. This problem is solved by the development of superplasticizers, high range water reducers. Superplasticizers are surface active agents. These modify the surface charges on the cement particles and

thus make them disperse. Entrapped water is released. Thereby, the consistency and flow ability is increased. These chemical admixtures are active for certain period of time, after which their effect is over and the cement paste starts stiffening. Superplasticizers have varied reactivity, depending upon their chemical configuration and molecular weight. Their reactivity or ability to disperse cement particles also depends upon the type of cement used. It is seen that one type of cement does not behave in the same way with different superplasticizer and one superplasticizer does not behave in the same way with different cements [1]. It is a dilemma and headache for the

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superplasticizer producers.

In the last decades, much work has been done on the superplasticizers, specifically with the development of high strength, high performance concrete. However the mechanism of interaction of superplasticizer is far from being understood. Besides, there are significant disagreements regarding the mechanisms by which they act.

The superplasticizers start their interaction in the fresh state immediately after mixing. This work is focused on the rheology properties of cement paste with the addition of superplasticizers. The properties studied are dispersion of cement particles with time, measurement of zeta potential, flow ability by measuring the spread on turntable, yield stress and viscosity.

2. MATERIALS

2.1 Superplasticizer type

Superplasticizers are classified in four basic groups:
Modified lignosulfonates (MLS)
Sulfonated melamine formaldehyde condensate (SMF)
Sulfonated naphthalene formaldehyde condensate (SNF)
Polycarboxylate ether (CE)
The chemical formulas are shown in Fig. 1.
The superplasticizers used in this work were:

• Lignosulfonate-based, Borresperse CA, Borregaard Lignotech, Norway. Powder with 100% active material, molecular weight: 6028

• Sulfonated melamine formaldehyde condensate, Peramin F, Perstorp Speciality Chemicals AB, Sweden. Solution with 34-36% active material, molecular weight: 28511

• Sulfonated naphthalene formaldehyde condensate, Cementa Melcrete, Cementa AB, Sweden. Solution with 36% active material, molecular weight: 1269

• Polycarboxylate-based, Glenium 51, Modern Betong, Sweden. Solution with 35% active material, molecular

Sodium lignosulfonate

Sodium salt of sulfonated naphthalene formaldehyde

Sodium salt of sulfonated melamine formaldehyde
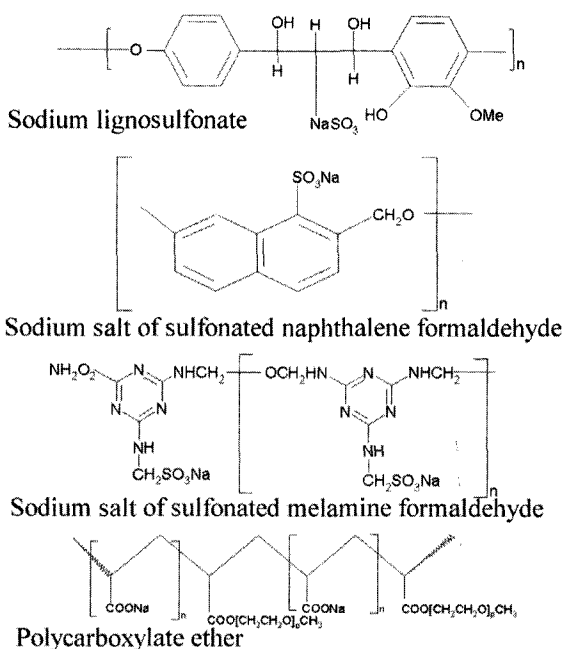
Polycarboxylate ether

Fig. 1 - Chemical formulas of superplasticizers [2].

weight: 42299

The dosage of superplasticizers (SP), mentioned in this study is calculated to the mass of cement. Mass of SP ($\approx$35 wt % solution melamine, naphthalene and polycarboxylate) and in solid form (lignosulfonate) to dry mass of cement. Hence, a dosage of 1% of a SP in solution ($\approx$35 wt %) is comparable to a dosage of 0.3% of a SP in solid form.

2.2 Cement type

Two types of cement have been used; Low-alkali cement, Slite, which will be called Cement A, and Building cement, Skövde, which will be called Cement B. The cements were supplied by Cementa AB, Sweden. The compositions and properties for the cements were supplied by the manufacturer, and are shown in Tables 1 and 2.

Table 1 - Cement compositions and properties		
	Cement A	Cement B*
CaO [% by mass]	64.8	61.5
SiO_2 [% by mass]	22.3	18.4
Al_2O_3 [% by mass]	3.4	4.9
Fe_2O_3 [% by mass]	4.3	2.9
MgO [% by mass]	0.8	1.2
Na_2O [% by mass]	0.1	0.1
K_2O [% by mass]	0.6	1.2
SO_3 [% by mass]	2.4	3.3
LOI [% by mass]	0.5	5.1
Of CO_2 [% by mass]	-	4.7
Chromate [mg/kg]	<2	<2
C_3A [% by mass]	1.8	8.0
C_2S [% by mass]	22.0	10.8
C_3S [% by mass]	55.7	50.9
C_4AF [% by mass]	13.2	8.0
Density [kg/m^3]	3211	3080
Spec. surface area [m^2/kg]	320	462
Binding time [min.]	129	143

Cement B contained 12% ground lime.

Table 2 – Particle size distribution							
[μm]	1	2	5	8	15	32	63
Cement A [%]	6.3	14.3	26.8	35.7	52.4	79.6	100
Cement B [%]	7.5	17.6	31.5	41.7	58.6	82.4	99.2

3. TEST PROCEDURES

3.1 Molecular weight determination

The molecular weights for the superplasticizers were determined by Perstorp AB, Sweden, using a gel permeation high performance liquid chromatography set-up. The HPLC system consisted of a pump, RI-detector, GPC data system, auto sampler, injector with a 20 µl loop. The colon type used was an Ultrahydrogel 250, 7.8x300 mm. As eluent 3g NaCl per litre HPLC water (Grade 1, ISO 3696) was used. The flow was set to 0.7 ml/min. 0.2 g of sample were mixed with 10 ml eluent. The mixture was

shaken for 30 min., followed by a filtration step and was then transferred to an auto sampler vial. The calibration was made with polysaccharides with the following molecular weights: 180, 738, 5800, 11800 and 100000.

3.2 Dispersion of cement particles

How the flocculation of cement particles in water and the dispersion is influenced by superplasticizers can easily be demonstrated through simple sedimentation experiments. These experiments were conducted in glass-tubes with a height of 1.5 m and an inner diameter of 28.3 mm. One hundred fifty g cement was stirred with 900 ml water and 0.5% superplasticizer to the cement mass. The height of the clear supernatant water was measured at particular time intervals.

3.3 Fluidity

Fluidity was measured on cement mortars made with a cement-to-sand ratio of 1 to 3. Sand used was standard sand 1, 2, 3. The water-to-cement ratio was 0.40. The mortars were made according to the SS137126.

The fluidity was evaluated by a flow test immediately after mixing, after 15, 30 and 45 minutes. Flow was measured at 20°C by the pull out spread of the mortar from a cone of top diameter 70 mm, bottom diameter 100 mm and height 60 mm after 15 turntable strokes. The spread was the average of two perpendicularly crossing bottom diameters.

3.4 Viscosity and yield stress

The viscosity and the yield stress as defined by the Bingham model were evaluated using a cone and plate rheometer. The rheometer used was of a type called CVO 200 High resolution, manufactured by Bohlin Instruments, UK. The cone diameter was 40 mm, with a cone angle of 4°. The samples were placed on the plate, and the cone was lowered so that a gap of 0.8 mm between the cone and the plate were achieved. Before measurements a pre-shear procedure was applied, to homogenize the sample, 20 seconds at a shear rate of $70s^{-1}$. The water-to-cement ratio (w/c) for the cement pastes was 0.30 in all experiments. During measurement the rheometer was programmed to perform a 10-step increase of the shear rate ranging from 0.0716 to 50 s^{-1} and back again to complete a full cycle.

3.5 Zeta potential measurements

The zeta potential was measured using an AcoustoSizer from Matec Applied Sciences, USA. The AcoustoSizer utilizes the electrokinetic sonic amplitude or ESA effect. Charged particles exposed to an alternating electric field in a solution generate sound waves. The frequency range is from 0.300 to 11.150 MHz, and gives a dynamic mobility distribution of particles in the size range from about 0.1 to 10 μm. The relation between the ESA signal and the dynamic mobility of the particles, μ_d, is seen in Equation (1) [3].

$$ESA(\omega) = A\ (\omega)\ \phi\ (\Delta\rho/\rho)\ <\mu_d> \qquad (1)$$

where ω is the angular frequency of the applied field, A is an instrument factor, ϕ is the volume fraction, $\Delta\rho$ is the

density of the particles minus the density ρ of the solvent, and $<\mu_d>$ is the particle-averaged dynamic mobility. The model used by the AcoustoSizer relates the dynamic mobility to the particle size and zeta potential.

For thin double layers, μ_d can be related to the ζ-potential using the formula by O'Brien *et al.* [4] Equation (2).

$$<\mu_d> = (2\varepsilon_r\varepsilon_0\zeta/3\eta)G(\omega a^2/v)[1+f(\lambda, \omega)] \qquad (2)$$

Here, ε_r is the dielectric constant of the solvent, ε_0 is the permittivity of free space, a is the particle radius, η is the viscosity and v $(= \eta/\rho)$ is the kinematic viscosity. The G factor represents the effect of inertia forces, and varies between 0 and 1. The quantity λ is called the surface conduction parameter because it is related to the conductance of the double layer.

Often the AcoustoSizer failed to find a zeta-potential and particle size distribution (using Equation (2)) due to convergence problems. This is most probably due to the very broad size distribution exhibited by the cement particles, but there might also be some problem with particles sticking to the electrode [5], which tend to distort the phase angles.

Due to the above-mentioned convergence problems, we only report an "apparent" zeta potential, which is calculated from the Smoluchowski equation, Equation (3).

$$\mu_d = \frac{\varepsilon_r\varepsilon_0\zeta}{\eta} \qquad (3)$$

This calculation is based on a single average dynamic mobility measured at an electric field frequency of 0.3 MHz. At such low frequencies, the effect of inertia forces is often unimportant (G=1), but not in this case. A comparison between the "fitted" and the "apparent" zeta-potential tells us that the "apparent" zeta-potential is about three times lower than the fitted zeta-potential. This discrepancy can be ascribed to the inertia of the cement particles (G≈0.3 in Equation (2)).

All Zeta potentials were measured using the following method:

Cement (233.3g) and deionised water (350g) were mixed in a beaker. In the cases when a superplasticizer was present, it was mixed with the water prior the cement addition. To prevent formation of cement aggregates, especially when no superplasticizer was present, a rod emitting ultrasonic sound was immersed in the slurry for 5 min. The cement slurry was then transferred to the measuring cell and the temperature was set to 25°C. The conductivity and pH of the slurries were monitored. The slurry was stirred with a speed of 450 rpm. The time between mixing of the cement with water and the measurement was 30 min.

For background correction the cement slurries were centrifuged for 10 minutes at 10000 rpm, and the supernatant fluids were used as background medium.

4. TEST RESULTS AND DISCUSSION

Portland cement particles have a strong tendency to flocculate when mixed with water [6]. This tendency is the result of several types of interactions: van der Waals interaction between particles; electrostatic interactions

between sites bearing opposite charges, and strong interactions (or bridging) involving water molecules or hydrates [7]. Superplasticizers are adsorbed on the hydrating cement particles. This could decrease flocculation in at least three ways;

1. Increase in zeta potential; if all the particles carry a surface charge of the same sign and magnitude, they will repel each other, and will thereby disperse.
2. Increase in solid liquid affinity; if the particles are more strongly attracted to the liquid than to each other; they will tend to disperse.
3. Steric hindrance; the oriented adsorption of a non-ionic polymer can weaken the attraction between solid particles.

The hydration process leads to the formation of open
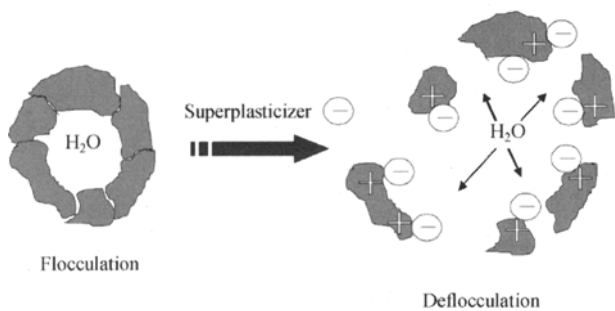
Fig. 2 – Flocculation of cement particles [8].

network voids Fig. 2, [8]. These particles are deflocculated by the addition of superplasticizers.

4.1 Influence of cement type

It is seen that the flocculation and deflocculation vary with the type of cement and the type of superplasticizer. To explain this phenomenon, first the role of different clinker minerals and the fineness of cement on the hydration process are discussed.

Cement is a complex mixture of inorganic compounds, mainly calcium silicates, calcium aluminates, calcium aluminoferrite, and calcium sulfate- ground together to varying degree of fineness. Some cement can also contain fillers, such as limestone in the case of Cement B in this experiment, or pozzolanic materials (blast furnace slag, silica fumes, or fly ash). The influence of cement fineness on the amount of superplasticizer needed to reach certain level of workability in the case of concretes (or of fluidity in the case of grouts) has been clearly established [9].The finer the cement, the higher the superplasticizer dosage required to achieve a given workability. The dispersion experiments (Fig. 3) performed show that the superplasticizers ability to disperse Cement B is less than for Cement A due to the fineness of the cement particles (462 m^2/kg for Cement B and 320 m^2/kg for Cement A). For the reference samples, it is seen that Cement A has a higher sedimentation rate due to the overall larger particle sizes.

The zeta potential measurements, shown in Figs. 4 and 5, revealed that particles of Cement B are negatively charged, thus some electrostatic repulsion can occur between the particles, decreasing the flocculation. Cement A particles on the other hand was close to neutral, promoting flocculation and sedimentation.

Because of the irregularities in the crystal structure, hydration of C_3S and C_3A is much faster than C_2S. It produces

high early strength, high heat of hydration, whereas C_2S is slow hardening and has low heat of hydration. C_3A hydrates spontaneously and forms ettringite with calcium sulfate (gypsum). Thus the higher the amount of C_3S and C_3A, the higher the degree of hydration will be, and consequently a higher early strength will be achieved. The C_3A contents of Cement A and Cement B is 1.8 and 8.0 respectively.

The addition of limestone, $CaCO_3$, accelerates the hydration process of C_3S especially at the early age (Cement B contains 12 % grounded lime). This accelerating effect may be related to a modification of the hydrating C_3S surface and its nucleating effect [10-12]. During hydration, the C_3A of the
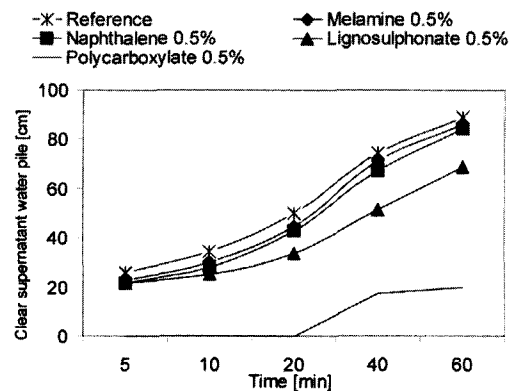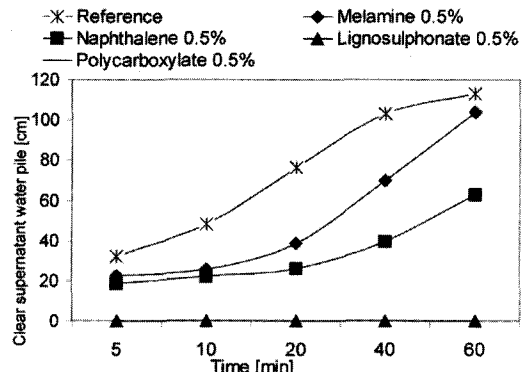
Fig. 3 – Heights of the clear supernatant water pile for cements with different superplasticizers. Upper graph for samples with Cement A. Bottom graph for samples with Cement B. Dosage of SP's are 0.5 mass % of active material to cement mass.
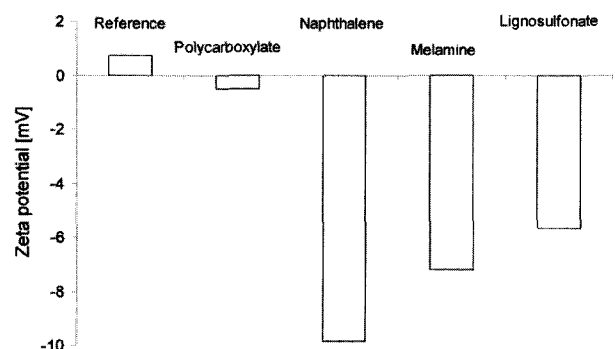
Fig. 4 – Zeta potential for slurries prepared with Cement A (40% cement by mass) and superplasticizer. The dosage of polycarboxylate, naphthalene and melamine was 1% of the cement mass and 0.3% for lignosulfonate. The results are based from three measurements for each data point. The largest standard deviation was 0.202. The pH for the slurries ranged from 12.4 to 12.6.
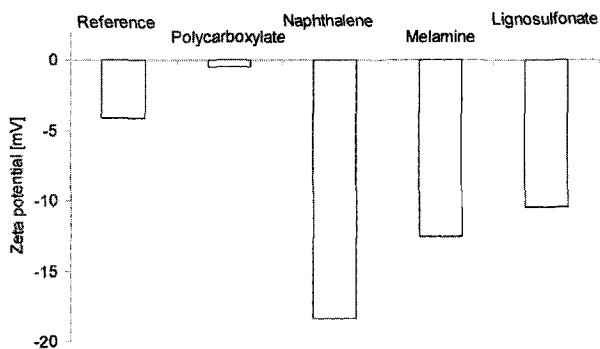
Fig. 5 – Zeta potential for slurries prepared with Cement B (40% cement by mass) and superplasticizer. The dosage of polycarboxylate, naphthalene and melamine was 1% of the cement mass and 0.3% for lignosulfonate. The results are based from three measurements for each data point. The largest standard deviation was 0.153. The pH for the slurries ranged from 12.5 to 12.7.

clinker reacts with the $CaCO_3$ to form calcium carboaluminate, whose structure and properties present analogies with the cement equivalents, calcium mono and tri sulfoaluminates.

It can thus be inferred that the reactivity of cement does not only depend upon the chemical composition of the cement clinker but also on the mineralogical composition, specifically on the ratio of C_3S /C_2S (2.5 for Cement A and 4.7 for Cement B). The higher the ratio of C_3S /C_2S, the higher the degree of hydration will be, and thus higher early strength. Degree of hydration also depends upon the fineness of the cement. Higher is the specific surface area, faster will be the hydration, and consequently this will lead to higher early strength.

The fluidity experiments clearly show that lower spread values are obtained with cement type B (Figs. 6 and 7), which are in agreement with the above mentioned conclusions.

Figs. 8 and 9 show the yield stress and viscosity change with time for cement pastes made with different superplasticizers for Cement A and Cement B respectively. Both the yield stress and the viscosity increase with time. The higher viscosity and yield stress for pastes prepared with Cement B is due to the fact that less dispersion of cement particles makes less water available as lubricant. Another factor is that Cement B contains 12 % ground lime, which accelerates the hydration process by providing nucleus sites. Additionally Cement B has a larger specific surface area, C_3S /C_2S ratio, and C_3A content than Cement A. The reactivity towards hydration for Cement B is thus larger, resulting in lower spread values and higher yield stress and viscosity compared to Cement A.

4.2 Influence of superplasticizer type

Superplasticizers are adsorbed on the surface of cement particles, which deflocculates. The dispersion mechanism is dependent upon the type of superplasticizer adsorbed on the surface.

Basically, there are two types of dispersion mechanisms: electrostatic repulsion and steric hindrance [13].

It is seen from Figs. 4 and 5 that the zeta potentials for the slurries containing sulfonated superplasticizers are very negative. Whereas the zeta potential for the reference slurry prepared with Cement A (Fig. 4) is slightly positive. When a polycarboxylate-based superplasticizer was used the zeta

potential shifted to slightly negative (-0.514 mV), but not as negative as when sulfonated superplasticizers were used (melamine, naphthalene and lignosulfonate). The highest negative zeta potential obtained with Cement A was with naphthalene (Fig. 4). The reference slurry prepared with Cement B gave a negative zeta potential, and was almost shifted to zero when a polycarboxylate superplasticizer was used (Fig. 5). The same trend in the zeta potential can be seen for Cement B as for Cement A. The zeta potentials obtained with the sulfonated superplasticizers were also more negative when using Cement type B than with Cement A. The variation in pH for the different cement slurries was small, ranging from 12.4 to 12.7.

The relatively high negative zeta potentials obtained when superplasticizers with a sulfonic group, lignosulfonate, naphthalene and melamine, were used suggest that the dispersion mechanism of cement particles is mainly controlled by electrostatic repulsion between negatively charged particles. The zeta potentials obtained when using a polycarboxylate-based superplasticizer are close to zero. This proves that the mechanism by which cement particles are dispersed is not attributed to electrostatic repulsion. Dispersion of cement particles in this case must be due to
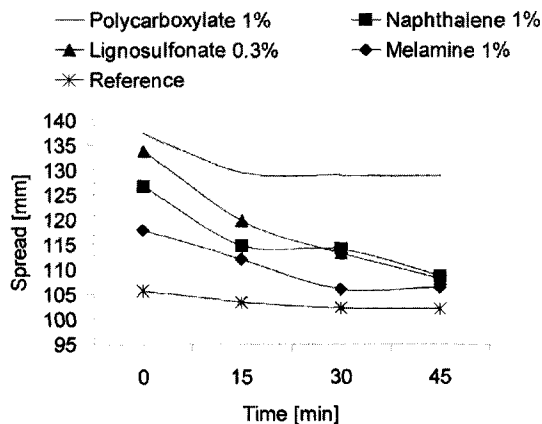

Fig. 6 – The consistency for different mortars, with time for Cement A. The water-to-cement ratio was 0.40 and the cement-to-sand ratio was 0.33. Dosage of superplasticizer was 1% with respect to cement mass, except for lignosulfonate 0.3%.
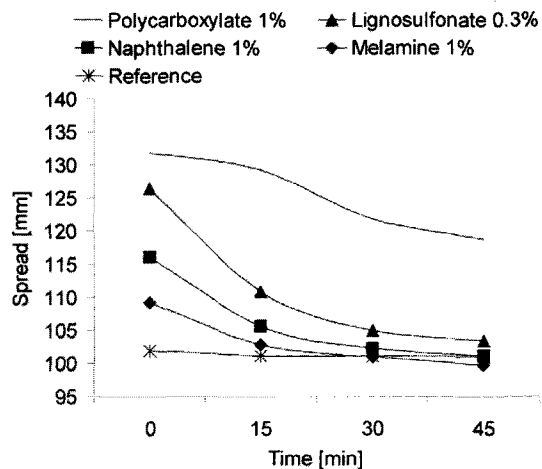

Fig. 7 - The consistency for different mortars, with time for Cement B. The water-to-cement ratio was 0.40 and the cement-to-sand ratio was 0.33. Dosage of superplasticizer was 1% with respect to cement mass, except for lignosulfonate 0.3%.
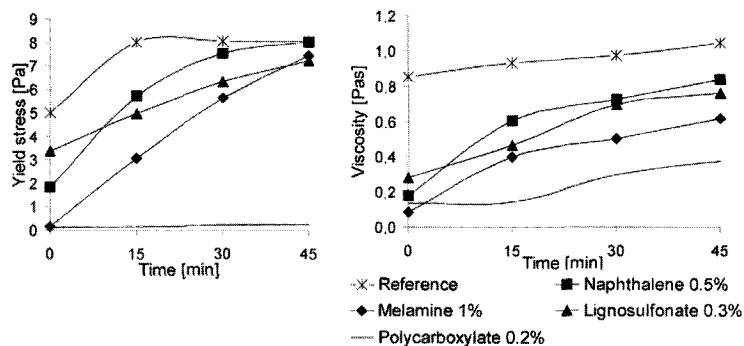
Fig. 8 – Yield stress and viscosity change with time for pastes prepared with Cement A. The water-to-cement ratio was 0.30.
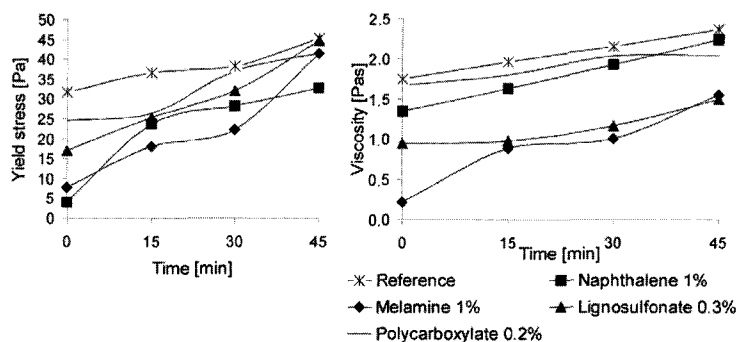

Fig. 9 – Yield stress and viscosity change with time for pastes prepared with Cement B. The water-to-cement ratio was 0.30.

steric effects. These results suggest that the dispersion of cement particles with a polycarboxylate-type SP and the other types of SP's is different.

The fact that sulfonated superplasticizers give rise to a higher negative zeta potential than polycarboxylate acid-based superplasticizers are also reported by Uchikawa et al. [14].

The polycarboxylate polymer has a high molecular weight (42 299). It is made up of a backbone, with carboxylic groups, and polyoxyethylene side chains. These long side chains contribute to the role of steric hindrance in the case when polycarboxylate superplasticizer is used. It is believed that the adsorption of this kind of polymer on cement particles occurs via carboxylic acid groups [15]. The lignosulfonate, sulfonated melamine and sulfonated naphthalene-type superplasticizers have a lower molecular mass than the polycarboxylate type (6028, 28511 and 1269 respectively) and have no long side chains.

Andersen and Roy (1987) have reported that the SP (sulfonated polymers of naphthalene, melamine and polystyrene) with largest molecular weight gives the largest negative zeta potential, and is therefore concluded to have higher dispersing capability [16]. The absence of long side chains provide the smaller sulfonated polymers with a higher charge density than the heavier polycarboxylate type polymer, therefore the electrostatic repulsion is more pronounced.

The superplasticizer's ability to disperse Cement B is less than for Cement A. This is not only due to the fact that the specific surface area is larger for Cement B than for Cement A (462 m^2/kg and 320 m^2/kg respectively). It is also related to the differences in chemical compositions of the two cements.

A cement particle may contain cement minerals including alite (C_3S) and belite (C_2S), as well as aluminate phase (C_3A), ferrite phase (C_4AF), alkali sulfate, f-CaO and gypsum in interstitial phase. The admixture is not evenly adsorbed on cement particles but rather is adsorbed according to the kind of cement mineral. It is adsorbed less on alite and belite, while adsorbed much more on C_3A, C_4AF and f-CaO [17].

Cement B has a much higher C_3A content than Cement A (9.0 and 1.8 respectively) which can further explain why the superplasticizers ability to disperse Cement B is less than for Cement A. Higher C_3A content leaves a lower amount of superplasticizer in the pore solution. Superplasticizer molecules in the pore solution can act as an additional repulsive barrier between cement particles [18].

Now, when it is established why the dispersion of the two cement types is different the same reasoning can be applied to explain the difference in fluidity. It is seen that the fluidity of mortar and cement paste prepared with Cement B is lower than for Cement A. Both the fluidity of mortar determined by the flow test (Figs. 6 and 7) and the rheology experiments (Figs. 8 and 9) on cement paste are in agreement, samples made with Cement B are less fluid. As stated earlier the superplasticizers ability to disperse and release entrapped water is less for Cement B. Thus, less water is available to act as lubricant between cement particles.

Amongst the superplasticizers used, it is seen that the polycarboxylate-type is the most effective. This is clearly seen in the sedimentation experiments (Fig. 3) where the clear supernatant water pile was measured, polycarboxylate-type superplasticizer gave the shortest supernatant water pile. In the fluidity measurements of mortar with the flow test, it is seen that for both cement types the most fluid mortars were the ones with polycarboxylate superplasticizer. In the rheology measurements, the dosage of polycarboxylate had to be decreased to 0.2 %, as a higher dosage produced bleeding, which caused slipping between the sample and the cone. However the paste made with Cement A and 0.2% polycarboxylate had the lowest yield stress and viscosity values (Fig. 8).

5. PROPOSAL OF ADSORPTION MODEL OF SUPERPLASTICIZER ON CEMENT SURFACE

According to Andersen and Roy [16], any charge adsorbed directly on the cement surface is neutralized and only negative charges positioned in the Stern layer (adsorption layer of organic admixture) contribute to the zeta potential. In the adsorption model proposed (Fig. 10) two polymers pictured will possibly be adsorbed, due to the differences in their molecular weights, more or less in "train" and "loop" formation with a small part of the ends of the polymers in "tail" formation. In the model, a comparison between a low molecular weight and high molecular weight polymer is made

Train-formation
Low molecular weight polymer

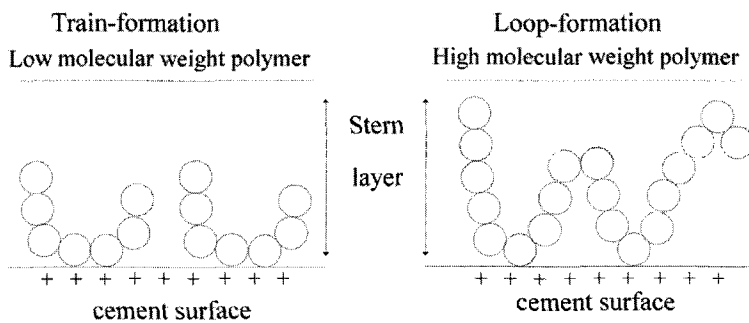Loop-formation
High molecular weight polymer

Fig. 10 – Model of polymer adsorption proposed by Andersen and Roy (1987) [16].
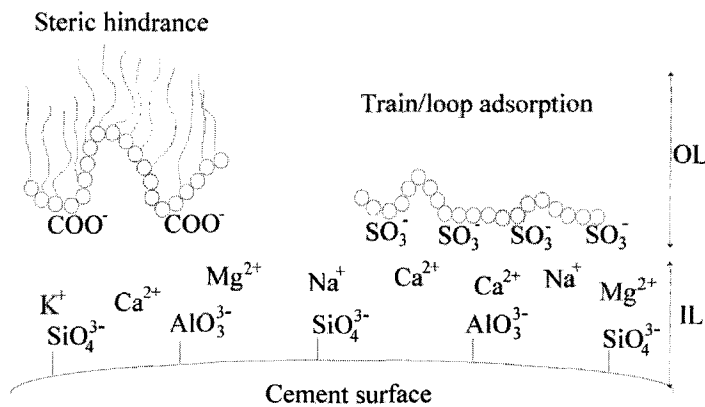

Fig. 11 – Adsorption model of superplasticizer molecules onto a cement particle.

with regard to how many of the polymer charges are neutralized by the adsorption.

In the model many of the charges in the low molecular weight polymer are assumed to be neutralized, while only a small part of the charges in the high molecular weight polymer are neutralized. The result of the model is that although less of the high molecular weight polymer is adsorbed it is still able to introduce more negative charges into the Stern layer. Anderson and Roy have concluded that the high molecular weight polymer, which gives a higher zeta potential, is therefore assumed to be a better dispersing agent than polymers which gives lower zeta potentials.

But the point that higher negative zeta potential provides higher dispersion does not fit well, as the dispersion of cement particles is not only due to electrostatic forces but also due to steric hindrance as in the case with non sulfonated superplasticizer (polycarboxylate acid).

The influence of ions in the pore solutions should also be taken into consideration, since the zeta potential for different cement types in water can vary from slightly positive to slightly negative. The adsorption of superplasticizer is therefore explained by Stern double layer formation (Fig. 11). It consists of two layers, an inner layer (IL) in which adsorbed molecules or ions are connected with the surface of a cement particle directly and have intimate arrangement with each other, and an outer layer (OL) in which adsorbed molecules or ions have a diffuse arrangement.

When cement is mixed with water, positive ions such as Ca^{2+}, Mg^{2+}, Na^+ and K^+ are dissolved into the solution, while the frame of SiO_4^{3-}, AlO_3^{3-} remains, leading to its surface with negative charge. Therefore, Stern IL consists

of positive ions and water dipoles and Stern OL of negative ions and water dipoles.

In this model the sum of positive charges in the IL has to be more than the sum of the negative charges in the OL. Because of a strong physical-chemical interaction between cement and water, it is reasonable to think that many water dipoles are present in both Stern IL and OL. In Fig. 11, the authors suggest a model for the superplasticizer adsorption onto a cement particle. When an admixture enters through competitive adsorption, only replacement in the Stern outer layer is involved. If many SO_3^- groups occur in a molecule as in the case of polymer, multipoint adsorptions are usual. Multipoint absorption is shown by train/loop formation. Sulfonated polymers introduce negative charges on the cement surface, and dispersion is attributed to electrostatic repulsion of cement particles. In the case with polycarboxylate there are no SO_3^- groups, and comparatively the molecular weight is higher than for sulfonated superplasticizers, the adsorption of polycarboxylate polymers does not give rise to high negative surface charges. The dispersion of cement particles is now attributed to steric hindrance, since polycarboxylate type SP has long hydrophilic side chains which are extended into the pore solution.

6. CONCLUSIONS

The action of MLS, SMF, and SNF is due to their adsorption onto the cement grains, which then acquire an electrostatic charge. This leads to the dispersion of the cement particles and subsequently an increase in fluidity. The rate and amount of superplasticizer adsorption on cement compounds influence the rheology, setting and hydration mechanism. The fourth superplasticizer based on polycarboxylic ether polymers have long hydrophilic side chains that guarantees a steric type of repulsion, which keeps the cement particles separated even after the polymer molecule is covered by the initial hydration products.

Due to the wide variability in the chemical and physical properties of cements, different cements behave in different ways in the presence of the same superplasticizer. Among the chemical parameters of cement, which have been found to exert a major influence on the properties of superplasticized cement mixes, are the C_3A content, specific surface area, the morphology of the C_3A, the alkali content, and the form of calcium sulfate added to the clinker during grinding.

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