INFLUENCE OF SUPERPLASTICIZERS AND SLAG BLENDED CEMENT ON THE RHEOLOGY OF FINE MORTAR PART OF CONCRETE

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ABSTRACT

Rheological characterisation of the fine mortar part of concrete plays an important role in the development of self-compacting concrete, SCC. The flowability of SCC is controlled with the use of superplasticizers while the stability is controlled with addition of filler materials. A method to evaluate the influence of these chemical- and mineral additives on fine mortar rheology is presented. Five different superplasticizers are tested on fine mortars where blast furnace slag increasingly replaces cement. By this replacement of cement with slag the fineness as well as the surface chemistry of the total particle system is changed. Despite this fact no significant rheological effect of increasing slag amount can be measured. Neither can the surface-active superplasticizers distinguish any rheological difference depending on slag amount. There are however very clear and big differences in dispersing effect between the tested superplasticizers.

Key words: Rheology, Fine mortar, Blast furnace slag, Superplasticizer, Bingham model, Yield stress, Plastic viscosity.

1. Introduction

In the development of self-compacting concrete, SCC, an understanding of the fine mortar rheology is an important task. The most vital properties of fresh self-compacting concrete are the ability to flow under no other influence but of gravitational force while at the same time having sufficient stability against segregation.

The flowability of the concrete is achieved by use of a superplasticizer, which in rheology terms lower the yield stress, τ_0, according to the Bingham model, see Eq. 1. The other rheology parameter according the model, plastic viscosity, μ_{pl}, is the parameter that describes the stability of the fresh concrete. By increasing the amount of fine materials (fillers) the solid fraction of the fine mortar part of concrete increases and thus the fine mortar viscosity. Since the fine mortar can be considered as the liquid phase of concrete, the plastic viscosity of concrete is increased to a necessary level preventing segregation of coarse aggregate.

$$\tau_0 = \tau + \mu_{pl} \cdot \dot{\gamma} \quad (1)$$

where

τ_0 = Yield stress [Pa]
τ = Shear stress [Pa]
μ_{pl} = Plastic viscosity [Pa s]
$\dot{\gamma}$ = Shear rate [s^{-1}]

Evaluation of rheologically acceptable types of filler material and optimum types of superplasticizer can be made by measuring the rheology of the fine mortar part of concrete. This paper reports results from rheology measurements of fine mortar made for the purpose of evaluating the influence of different superplasticizers on cement that is increasingly blended with slag.

2. Methods and materials

The viscometer used in this investigation is a HAAKE Rotovisco 20. The measuring system consists of concentric cylinders where the outer cylinder originates from the standard measuring system HAAKE ZA 30. The inner cylinder is made according to the original ZA 30-bob except for a smaller diameter (24.83 mm instead of 27.83 mm for the original bob) and a serrated surface. The smaller diameter enables the maximum particle size (Dmax) to be 0.25 mm and still fulfil the criteria that states that Gap/Dmax ≥ 10. The surface of the inner cylinder is serrated in order to prevent a so-called slip surface to occur. A commonly accepted rule is that the roughness (asperities) should be in the size range of Dmax in the suspension. In Table 1 the geometry of the actual measuring system is shown and compared with criteria stated for scientifically accepted geometry [1].

To reach required repeatability and accuracy of results, first of all both the mixing equipment and mixing sequence have to be perfectly repeated for every test, see [2]. Secondly, the shear sequence during tests has to be exactly repeated. The reason is that mechanical dispersion of aggregate depends both of mixing intensity and of the way the fine mortar is sheared in the viscometer. The used shear sequence is shown in FIG. 1. Thirdly, regression according to the Bingham model should be made on the same shear rate interval every time since the registered flow curves show shear thinning behaviour of the fine mortars. The chosen shear rate interval is between 5 – 15 s^{-1}, see FIG. 1.

Table 1. Scientifically correct geometry vs. actual geometry.

Criteria	Actual
Ry/Ri ≤ 1.2	1.2
Ry-Ri ≥ 10 · Dmax	10.3· Dmax
h/Ri > 1	2.17
Asperities/Dmax ≥ 1	2

The three up- and down loops that forms the shear sequence are used to evaluate the stability of the fine mortar tested. A stable fine mortar normally shows a certain structural degradation or mechanical dispersion, during the three loops. Segregation however results in that a sediment layer reaches the bottom of the inner cylinder and thus higher and higher shear stresses are recorded.

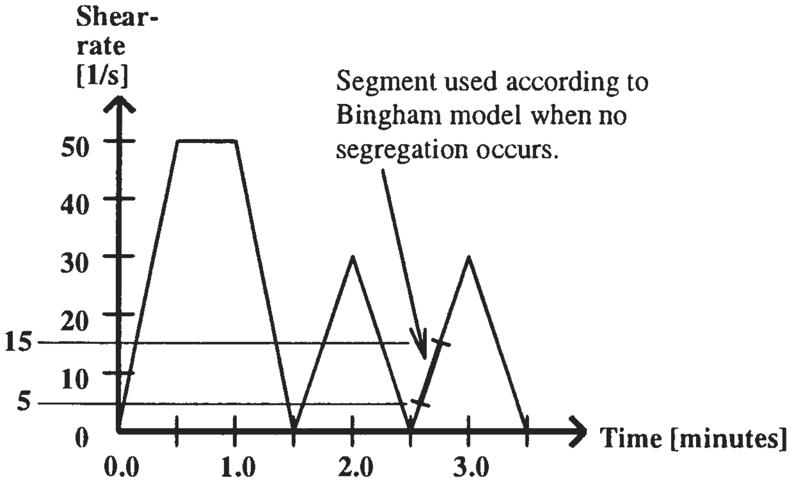

FIG. 1. Shear sequence used in rheology measurements.

The tested cement is a low alkali, sulphate resistant and low heat portland cement (ANL). It is tested in combination with a blast furnace slag (SLG). The characteristics of ANL and SLG are listed in Table 2. The fine aggregate used is a filter sand which is sieved to have a maximum particle size 0.25 mm. Particle size distributions of cement, blast furnace slag and sand are shown in FIG. 2.

Table 2. Tested cement, ANL, and blast furnace slag.

Chemical and physical data			
Cement		**Slag**	
C_3S (%)	53	SiO_2 (%)	35.7
C_2S (%)	23	Al_2O_3 (%)	10.5
C_3A (%)	1.6	CaO (%)	35.1
C_4AF (%)	14	MgO (%)	14.5
SO_3 (%)	2.1	Amount glassy material (%)	97
MgO (%)	0.9	Density (kg/m^3)	2920
Alkali content as equiv. Na_2O (%)	0.47	Blaine (m^2/kg)	500
Density (kg/m^3)	3220		
Blaine (m^2/kg)	300		

Data of the tested superplasticizers are shown in Table 3. The five different superplasticizers are based on different active polymers. SP-1 and SP-2 represents traditional types of superplasticizers while SP-3 and SP-4 represents more recently developed admixtures. SP-5 is a very modern type of superplasticizer based on acrylic graft copolymers with functional sulfonic and carboxyl groups.

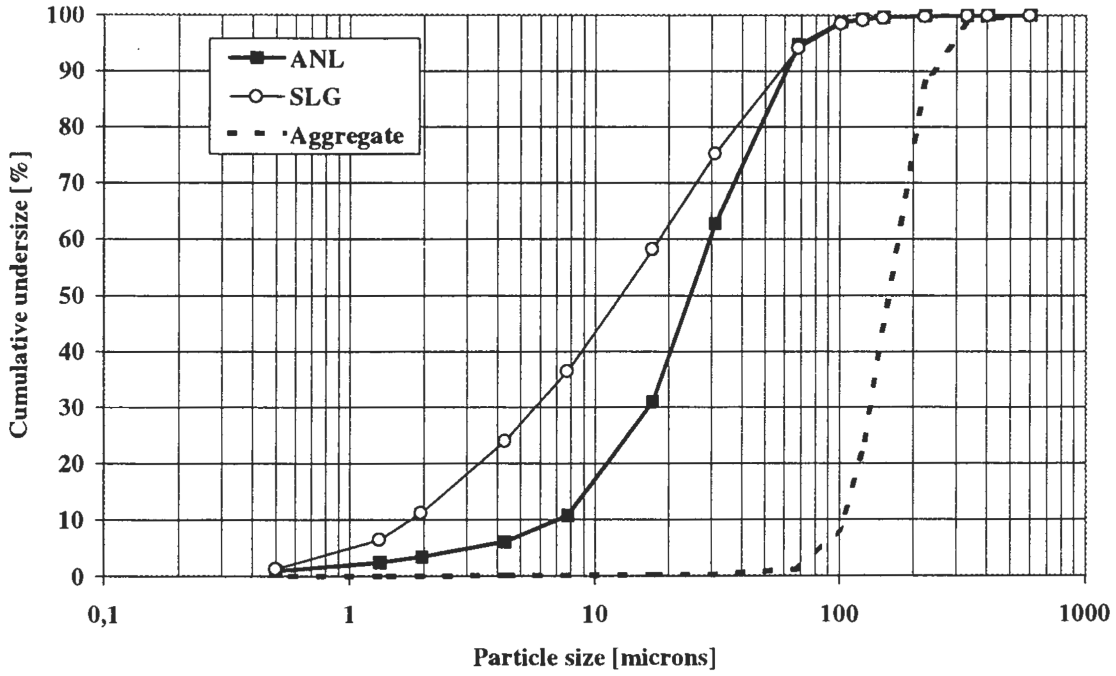

FIG. 2. Particle size distribution of tested materials.

Table 3. Tested superplasticizers.

Designation	Active component	Solid content [%]
SP-1	Sulphonated melamine and naphthalene formaldehyde condensate	35
SP-2	Sulphonated melamine formaldehyde condensate	35
SP-3	Vinyl copolymer in comb. with sulphonated melamine	20
SP-4	Copolymer of maleic anhydride and styrene	40
SP-5	Acryl Graft Copolymer	30

3. Results

All fine mortars here tested have constant cement plus slag content corresponding to 525 kg/m³ in concrete. The amount of slag is varied from 100 to 150 and finally 200 kg/m³ and thus the cement is reduced from 425 to 375 and finally 325 kg/m³. The aggregate content corresponds to a sand 0-8 mm fraction, which have 13 % material passing 0.25 mm sieve. The water to binder (cement+slag) ratio, W/B, is kept constant at 0.45 throughout the investigation. Superplasticizers are constantly dosed as liquid at 0.2 % of cement plus slag weight.

A typical flow-curve representing the measured shear stress versus applied shear rate for a complete shear sequence is shown in FIG. 3. Note the structural breakdown of aggregated particles during the first shear-rate loop and that the second and third loops coincide. The fine mortar tested shows no signs of particle segregation. Neither does the fine mortar show any time dependent behaviour since the up- and down-curve for the two last loops almost completely coincide.

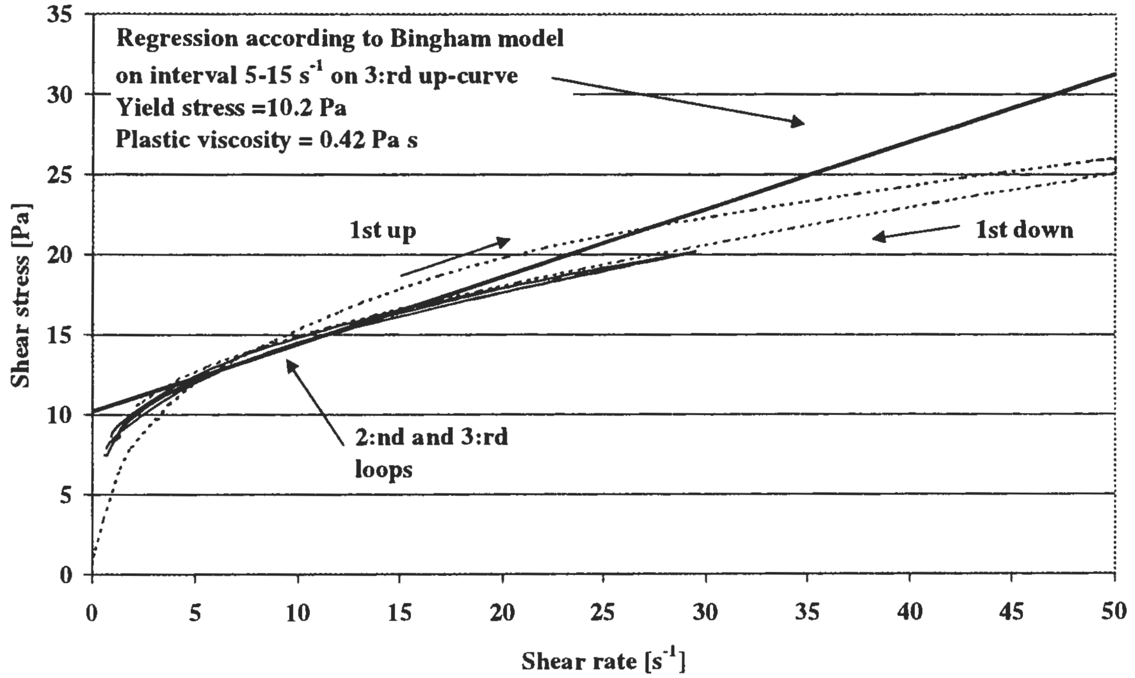

FIG. 3. Flow-curve representing a complete shear sequence.

The reference fine mortars with no superplasticizer added were tested three times each. The results are shown in Table 4 and Table 5.

Table 4. Repeatability of measurements of yield stress on reference fine mortars.

ANL	Slag	Yield stress [Pa]		
kg/m³	kg/m³	τ_0	Mean	Standard deviation
425	100	9.94		
425	100	10.03	10.0	0.045
425	100	10.00		
375	150	10.50		
375	150	10.18	10.3	0.191
375	150	10.16		
325	200	10.26		
325	200	10.44	10.5	0.286
325	200	10.82		

Table 5. Repeatability of measurements of plastic viscosity on reference fine mortars.

ANL	Slag	Plastic viscosity [Pa s]		
kg/m³	kg/m³	μ	Mean	Standard deviation
425	100	0.42		
425	100	0.43	0.42	0.009
425	100	0.42		
375	150	0.43		
375	150	0.42	0.43	0.004
375	150	0.43		
325	200	0.43		
325	200	0.42	0.44	0.036
325	200	0.48		

By replacing cement with slag the specific surface area of particles as well as the solid volume fraction of the fine mortar increases. Despite this fact both the yield stress and the plastic viscosity are nearly constant when the amount of slag increases. It has been reported earlier, see [3] and [4], that an increase in both cement and filler material fineness leads to an increase in yield stress and plastic viscosity. It has however several times been reported that replacing cement with slag improves workability of concrete [5, 6] and affects the rheology of pastes in a favourable way [5, 7, 8]. A possible answer to the observed behaviour can therefore be that the increase in particle fineness and solid volume fraction are balanced by the favourable glassy particle surface of slag as the cement is increasingly replaced by slag. It has also been reported in [9] that slag cement have a more highly negative zeta-potential compared to portland cement and thus results in better particle dispersion and higher fluidity of cement paste or mortar.

Because of the difference in surface chemistry of cement and slag it could be assumed that by adding superplasticizers it should be possible to measure a difference in rheology as the cement is replaced by slag. The results from tests where superplasticizers are added to the fine mortars are shown in FIG. 4 and FIG. 5.

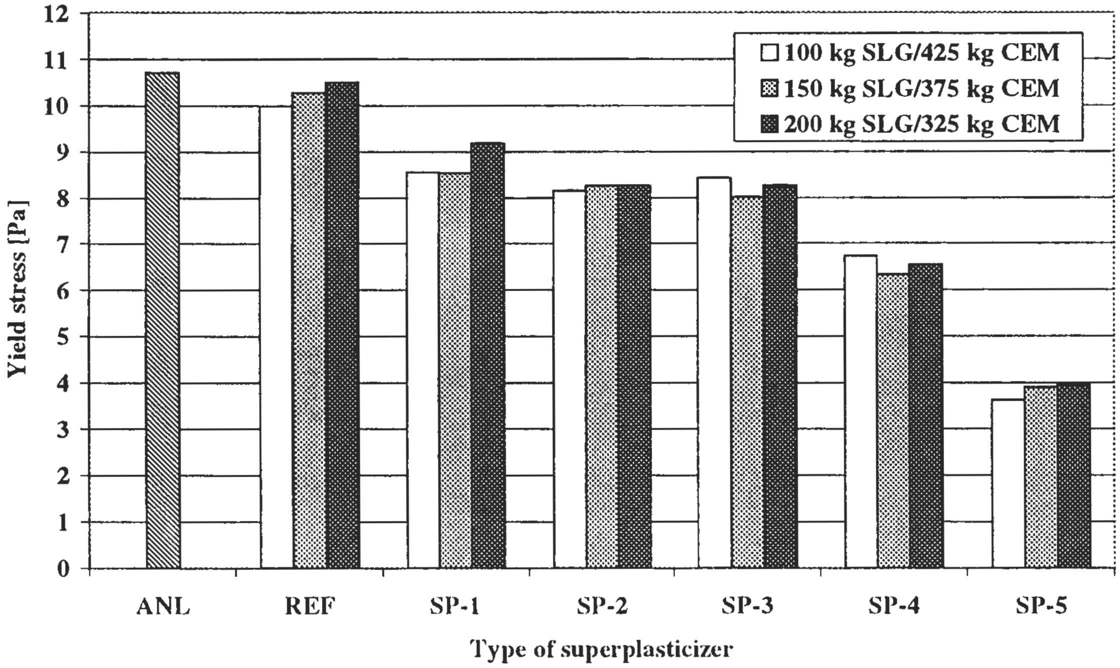

FIG. 4. Measured yield stresses for tested fine mortars.

When dosing the superplasticizers as liquid, i.e. not considering the solid polymer content, the superplasticizers designated SP-1, SP-2 and SP-3 show approximately the same efficiency. The reference yield stress of 10 Pa is reduced to just over 8 Pa when these superplasticizers are added. By adding the superplasticizer SP-4 and SP-5, yield stresses are reduced to approximately 6.5 Pa and 4 Pa respectively. It is however clear that no significant difference due to increased amount of slag was measured. It is however a very significant difference in efficiency between the tested superplasticizers.

The results of measured plastic viscosity show approximately the same trend as those of yield stresses in that no significant difference in measured values can be traced to amount of slag replacing cement.

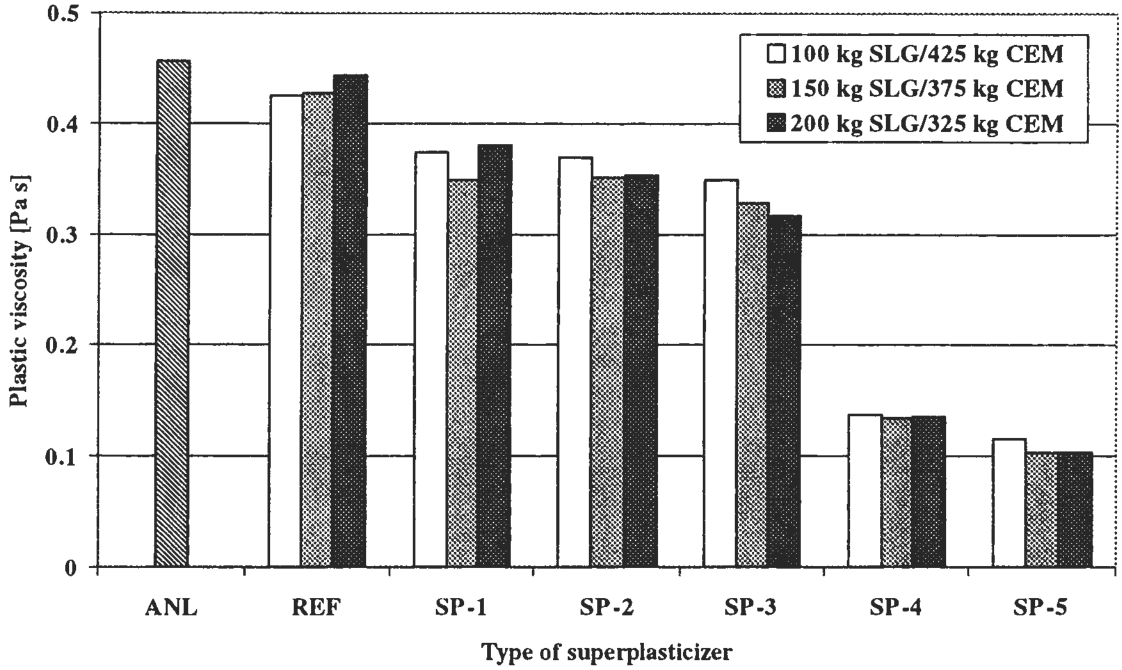

FIG. 5. Measured plastic viscosity for tested fine mortars.

In order to compare the superplasticizer efficiency in a more just way the ratios between superplasticizer effect on yield stress and plastic viscosity respectively and superplasticizer solids content have been calculated. In doing this it is assumed that the effect of superplasticizers are linearly dependent of superplasticizer dose. Even if this is not necessarily completely true in all cases, this ratio illustrates better the difference in efficiency related to type of surface-active polymers. The results are shown in FIG. 6 and FIG. 7.

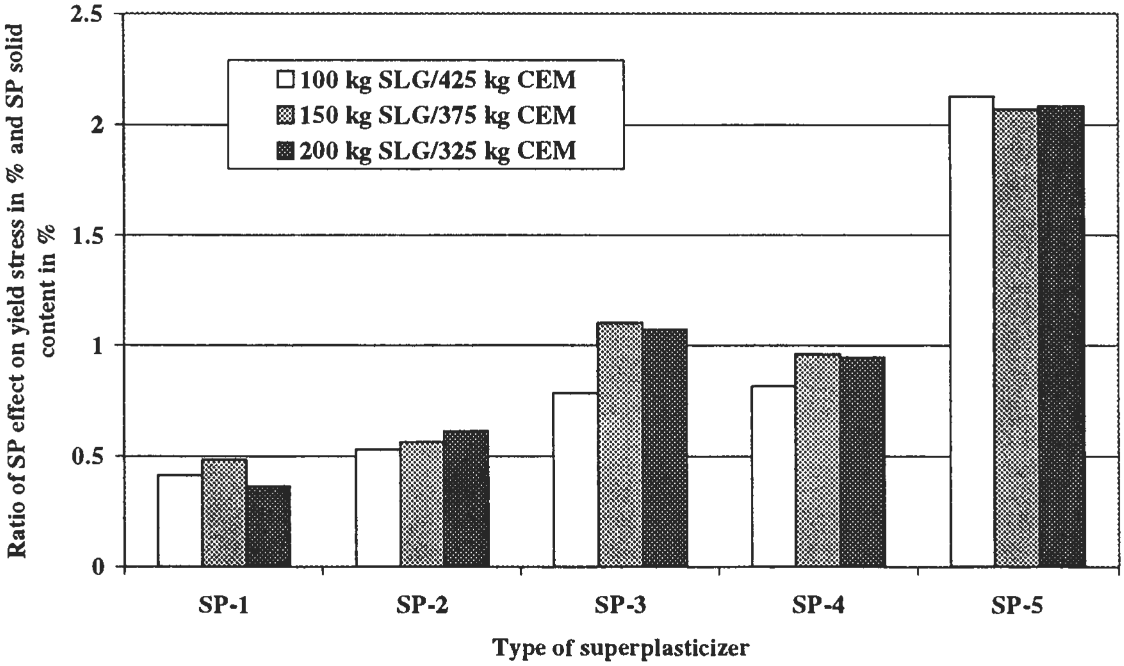

FIG. 6. Ratio of SP effect on yield stress in % and SP solid content in %.

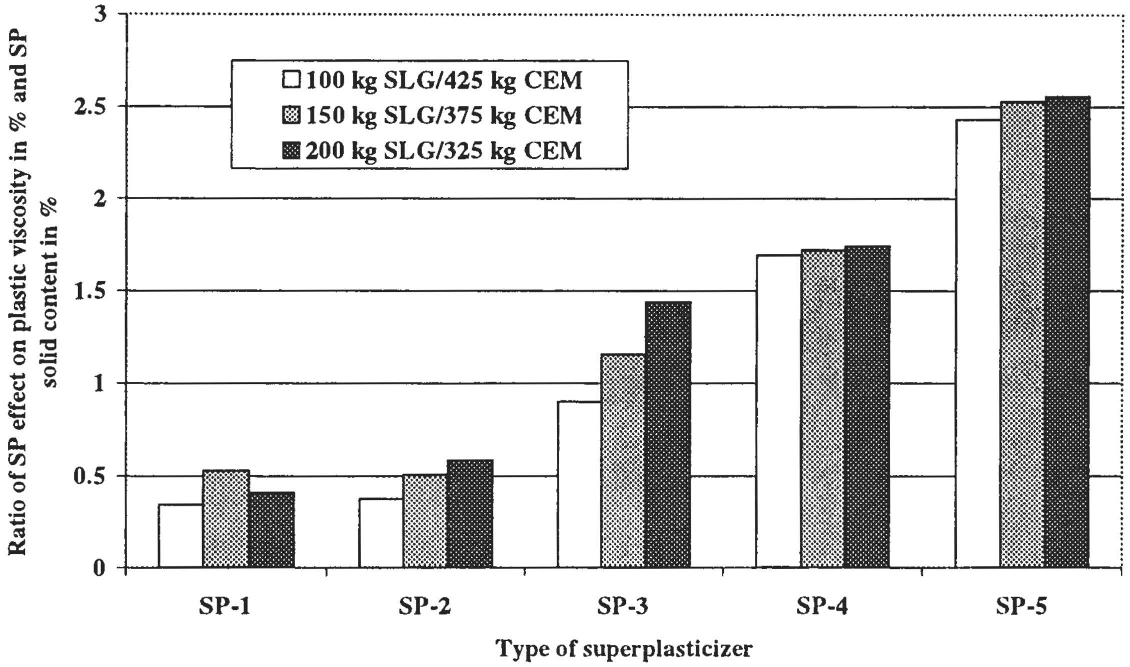

FIG. 7. Ratio of SP effect on plastic viscosity in % and SP solid content in %.

The only new information gained from the calculations resulting in FIG. 6 and FIG. 7, is the clear difference of superplasticizer depending on "generation". As mentioned earlier the superplasticizers designated SP-1 and SP-2 can be regarded as traditional ones based on a combination of naphthalene and melamine and naphthalene respectively. SP-3 and SP-4 belong to a later generation of superplasticizers while the most efficient superplasticizer, SP-5, is the latest developed admixture with further developed and much more effective active polymers.

4. Conclusions

When the tested cement is increasingly replaced by slag, the measured rheology parameters yield stress and plastic viscosity are left unaffected. By replacing parts of relatively coarse cement, i.e. ANL, having a Blaine-value of 300 m²/kg with a finer filler material, i.e. SLG, with a Blaine-value of 500 m²/kg, normally higher yield stress and plastic viscosity could be expected [3, 4]. It could also normally be expected that an increase in solid volume fraction of a particle suspension would lead to an increased viscosity [10]. By replacing a cement with density 3220 kg/m³ on mass-basis with a filler having a density 2920 kg/m³ it results in an increased solid volume fraction.

Slag has however some really positive properties that have been reported earlier. In [9] measurements of zeta-potential for slag cement was performed. Compared to normal Portland cement the slag cement has more highly negative zeta-potential and thus results in better particle dispersion and higher paste fluidity. In [6] it is theorized that improved workability of concrete containing ground granulating blast furnace slag is due to the smooth and dense surface of slag particles leading to that little if any water is absorbed by the slag particles during initial mixing.

Based on the present results and results previously reported it can be assumed that the increased solid volume fraction and particle specific surface respectively is balanced by the favourable properties of slag compared to normal Portland cement.
No one of five tested superplasticizers can display any preference of adsorbing on cement or slag particles and thus no significant change in rheology depending on ratio of slag and cement content can be measured.

The difference in efficiency is significant between the tested superplasticizers. In this case, three different generations of development can clearly be detected. SP-1 and SP-2, which are "traditional" types of superplasticizers based on naphthalene and melamine, show the least efficiency in reducing yield stress. SP-3 and SP-4 are more effective. They represent further development of synthetic polymers aiming both for higher efficiency and for more environmentally friendly polymers without formaldehyde. So does also SP-5, but this superplasticizer can be regarded as belonging to the latest generation of superplasticizers.

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