Effect of lignosulphonate plasticizer on rheological properties of ordinary portland cement with fly ash

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ABSTRACT

The effect of lignosulphonate as plasticizing admixture on Norwegian ordinary portland cement, EN 197-1 CEM I, compared to portland cement with fly ash, EN 197-1 CEM II/A-V and CEM II/B-V, was investigated to see a) the sensitivity of the performance of lignosulphonate to fly ash, b) the effect of increasing amount of fly ash on rheological properties, and c) the combined effect on rheological properties of increasing amount of fly ash and lignosulphonate in mortar.

The experimental work was performed according to factorial experimental design, so that the results could easily be analysed using multivariate data analysis.

The rheological properties were investigated by measuring rheological properties like viscosity and yield point in mortar using a ConTec 4 Rheometer. The measurements were performed 13 and 30 minutes after water addition.

INTRODUCTION

The trend in today's cement market goes towards increasing amount of blended cements. Including fly ash in ordinary construction cement has both economical and environmental advantages. The same goes for the use of plasticizing admixtures like lignosulphonate, where the increased workability of concrete will keep the need for cement at a minimum.

This investigation features an ordinary portland cement EN 197-1 CEM I, portland fly ash cement EN 197-1 CEM II/A-V (17% FA) and EN 197-1 CEM II/B-V (31% FA, produced in lab. scale). The plasticizing admixtures are a lignosulphonate plasticizer and a newly developed prototype lignosulphonate superplasticizer quality.

<u>Rheological measurements in cement-based materials</u>

The rheology of fresh cement paste depends on the rheology of the liquid phase, friction between grains and the bonds developing between grains due to hydration. Thus, the rheological properties of cement-based materials are dependent on the following[8] :

- Cement paste contains grains typically 10 - 100 microns.
- Mortar and concrete contain sand and aggregates.
- Silica fume and fly ash will influence the rheological properties.
- Water-cement ratio.
- Specific surface area.
- Mineral composition.
- Conditions during measurements.
- Temperature and time.

<u>Bingham plastic behaviour</u>

Cement paste and mortar are often described using the Bingham Plastic Model[4, 11].A liquid following this model is characterized by i) a certain amount of shear stress that is required for the liquid to flow, and ii) the liquid will display Newtonian flow once this limit is exceeded.

$$\tau = \tau_0 + \eta\dot{\gamma} \qquad (1)$$

where τ = shear stress, τ_0 = yield value, η = plastic viscosity and $\dot{\gamma}$ = shear rate.

This model is widely used because of its simplicity.

1.3 Concentric cylinder viscometers

The instrument used in this investigation is a concentric cylinder viscometer. The basics behind such instruments have been described by Mezger[11] and the ConTec Rheometer is described in detail by Wallevik[1], Wallevik and Gjørv[2] and Wallevik[17].This method assumes i) no slip between the cylinder and the sample, ii) laminar flow, iii) stationary flow and iv) that the properties of the sample are independent of time during the interval of measuring. The outer rotating cylinder is profiled with ribs in order to fulfil the assumptions for this type of viscometer. The inner cylinder will measure the torque at different angular velocities. This viscometer has a stationary inner cylinder that is designed in such a way that it doesn't affect the torque. For a Bingham plastic material, these measurement points will form a straight line. The slope, H, of this line gives the plastic viscosity, and the intercept with the ordinate, G, gives the yield point. It is thereby given that both H and G depend on the geometry of the viscometer. The Reiner-Riwlin equation is used to calculate the plastic viscosity and yield point from H and G. This calculation is explained by Wallevik[17].

Multivariate data analysis

A guide to multivariate data analysis is described by Martens[9]. Two bi-linear models were used in this investigation, Principal Component Analysis (PCA) and Partial Least Square Regression (PLSR).

In principal component analysis, the principal components (PC) are plotted, not the actual input variables. PCA is a bi-linear soft model (BLM) where the individual input variables are combined into a few principal components. Scores are the connection between the samples and the PCs, and loadings between the variables and the PCs. PCA is an easy way to interpret the results for someone with some knowledge on how the variables will interact with the samples. It is not required to have any formal training in statistics.

Partial least square regression is a similar type of model. The score and loadings plots from PLSR are interpreted in the same way as for PCA. However, the principal components are more directly relevant to the modelled property than for PCA. The regression coefficients obtained from PLSR give information on how much the x-variable influence the modelled property, y. Please note that these regression coefficients are scaled and centred. This type of modelling for analysis of experimental data is also shown by Svinning and Datu[15].

Lignosulphonate

Lignosulphonate is an organic macromolecule and a polyelectrolyte. One of its most pronounced properties is the ability to disperse particles in aqueous solutions. The commercial use of lignosulphonate as dispersant is summarized by Gargulak and Lebo[6]. It is used as a plasticizing admixture in concrete, i.e. to disperse the cement and fine particles in solution to improve the workability of dense suspensions like mortar or concrete. The mechanism of dispersing by lignosulphonate was studied by Gustafsson[7]. An overview of admixtures for concrete is given by Lea[5], and the chemical properties of lignosulphonate is given by Fredheim[10].

Fly ash

Fly ash is a by-product from the burning of coal in power plants. The ash is collected from the combustion gases and the particles form glass spheres 0 – 1 mm in diameter. The fly ash used in this investigation have d_{90}= 52,2 μm. The material composition is dependent on the non-combustible matter in the coal, and will also contain a small amount of carbon. Fly ash is used in cement and concrete as a pozzolanic material, i.e. it can form bonds in the system similar to the ones created during the hydration of cement. The use of fly ash in concrete is described by Lea[5] and Malhotra et al.[3].

EXPERIMENTAL

The rheological properties in mortar were investigated using a ConTec 4 Rheometer. The measurements were performed 13 and 30 minutes after water addition. The mortar is described in Table 1.

Two different lignosulphonate plasticizers were used: one ASTM class G plasticizer (Borresperse CASA [BspCASA]) and one superplasticizer prototype product, "LS5".

Three cements were used, with different levels of fly ash (FA).

- Norcem Standard (0% FA), SSA = 360 m^2/kg
- Norcem Standard FA (17% FA), SSA = 466 m^2/kg
- Norcem Standard FA with increased FA-content (31% FA), SSA = 444 m^2/kg

The experimental work was performed according to factorial experimental design. The design is shown in Table 2.

RESULTS AND DISCUSSION

Plastic viscosity and yield point

The plastic viscosity and yield point calculated from the experimental results from the Con Tec rheometer are shown in Fig. 1 and Fig. 2.

Table 1: Mix proportions for mortar.

	Classification	Amount
Cement/ binder	EN 197-1 CEM I 42.5 R, CEM II A-V, CEM II B-V	2500 g
Fly ash	EN 450 SSA=0.3436 m^2/g	Nill, 17% or 31% of total binder amount
w/(c+FA)		0.50
Aggregate	EN 480-1, d_{max}= 2.0 mm	7500 g
Admixture	Lignosulphonate	0.25 or 0.50 %sbwc (solids by weight of cement)
	Defoamer	TBP

Table 2: Experimental design

Run Order	LS5 [%sbwc]	BspCASA [%sbwc]	FA in cement [%]
1	0	0,25	0
2	0	0	0
3	0,25	0	0
4	0,5	0	17
5	0	0,25	17
6	0	0,5	31
7	0,25	0	17
8	0	0	17
9	0,5	0	0
10	0	0,5	0
11	0,25	0	31
12	0	0,25	31
13	0	0	31
14	0,5	0	31
15	0	0,5	17

Multivariate data analysis

Principal Component Analysis (PCA) gives scores and loadings for the samples and variables, a scores- and loadings plot for principal components 1 and 2 is shown in Fig. 3.

PCA give a visual impression of how the components and the properties interact. Variables situated close to each other in the loadings-plot will increase as one of them increases. Accordingly a variable on the other side of the axis will be inversely correlated. This is not necessarily a direct relationship between the variables, but it shows a correlation. The plots obtained by

PCA do not show any distinct groups other than the samples located nearby “LS5” which is the samples with high LS5-dosage. On other trends besides that the properties measured after 13 and 30 minutes are in the same area is visible. This is caused by the fact that all the parameters in the data set are important to the properties measured. From this analysis it can be seen that both the lignosulphonate plasticizers and the fly ash have a significant impact on the rheological properties of mortar.

Regression coefficients from Partial Least Square Regression (PLSR) are shown in Fig. 4.

The variable with the largest regression coefficient will be the one affecting the property that is modelled the most. Variables that point in the opposite direction in this graph, will have opposite influence on the property in question. It is clear that the lignosulphonate sample LS5 has the largest impact on viscosity at 13 minutes (v_13) and yield point (ys_13, ys_30). All three variables have similar impact on viscosity at 30 minutes (v_30).

The maximum explained variance from PLSR of the variables and the number of principal components included for this explanation is presented in Table 3. The data set consists of 15 samples and 7 variables.

Table 3: Results from PLSR of the data set collected.

Response variable	**Maximum explained varience [%]**	**Number of PC’s (latent variables)**
Viscosity 13 min	72	3
Viscosity 30 min	Not possible to model	
Yield stress 13 min	32	3
Yield stress 30 min	28	3

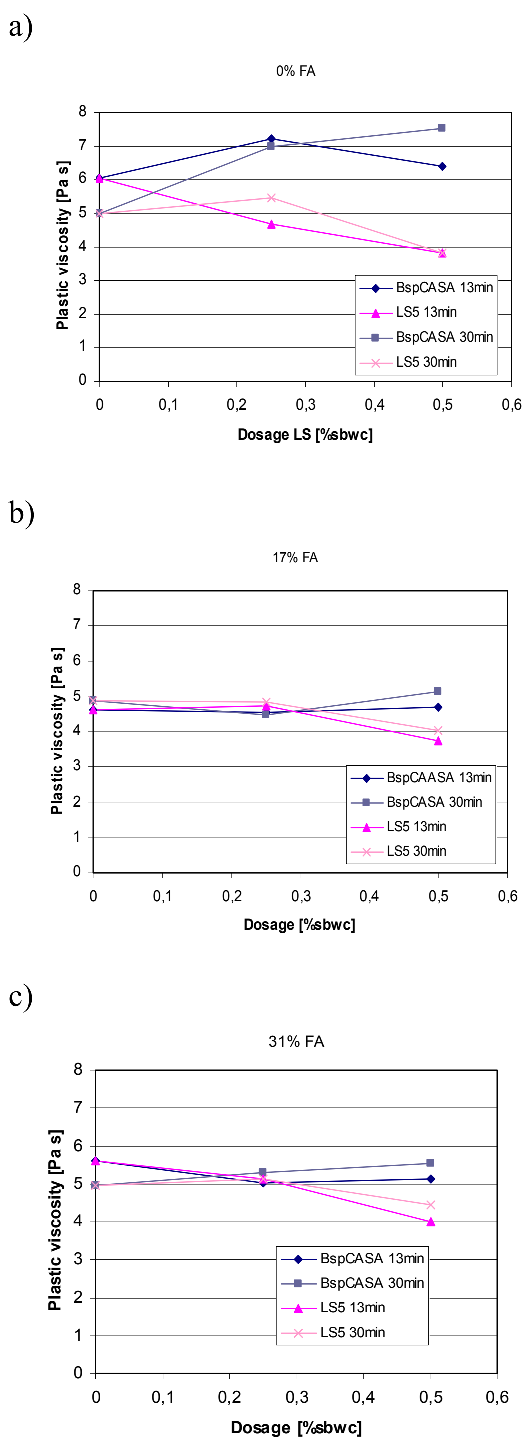

Fig. 1: Plastic viscosity for mortar with a) no FA, b) 17% FA and c) 31% FA.

a)

b)

c)

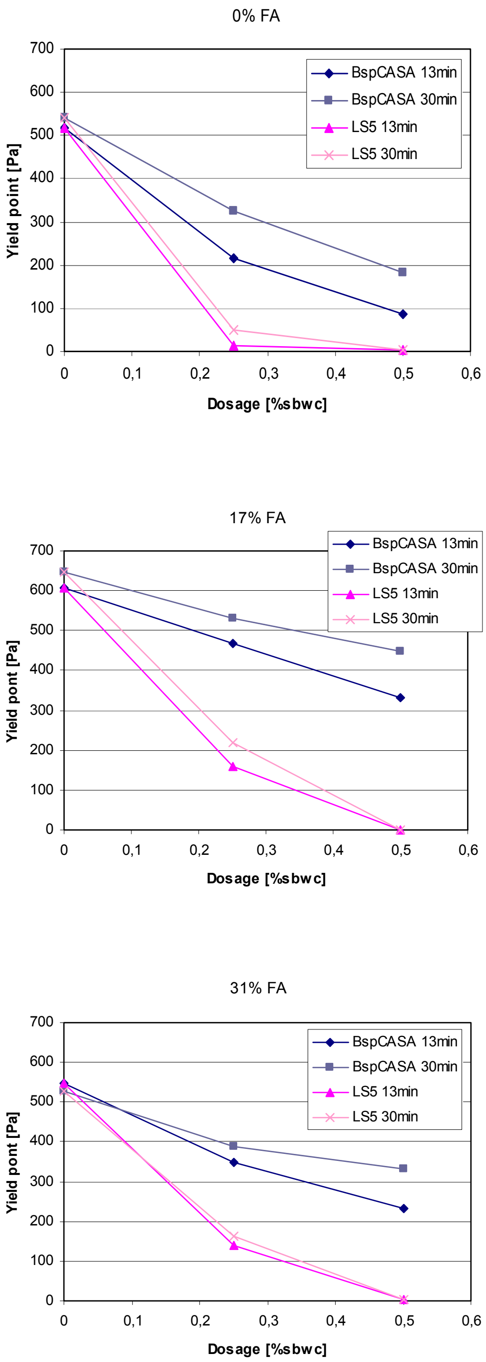

Fig. 2: Yield point for mortar with a) no FA, b) 17% FA and c) 31% FA.

<u>Discussion</u>

The results show that both the lignosulphonate samples and the fly ash have an important impact on the viscosity and yield point of mortar. Lachemi et al.[13] tested the properties of self-compacting concrete made with FA. They found that the slump flow increased when adding 40% FA in the cement and that the flow time from a V-funnel generally increased with the increase of FA content at constant w/(C+FA).

Addition of fly ash was expected to decrease the viscosity at high amounts, and to decrease the yield point[12].

When comparing the mortars without lignosulphonate, the plastic viscosity at 13 minutes after water addition is lower for mortars made with blended cements than for pure cement. After 30 minutes, the viscosity is the same for all mortars.

The yield point is the highest for mortars made with 17% FA, and within the same range for the other samples.

Addition of lignosulphonate was expected to decrease the viscosity at high dosages and to lower the yield point.

For the mortars made with pure cement, the viscosity increases when Bsp CASA is added, while it decreases when LS5 is added. This goes for both dosages and both times. For mortars made with blended cements, the plastic viscosity does not change significantly at the lowest dosage of lignosulphonate or for the measurements made at 13 minutes, while the high dosage at 30 minutes gives lower plastic viscosity.

The addition of lignosulphonate decreases the yield point a lot, and LS5 is more effective than Bsp CASA. The yield points are lower for mortar made from pure cement than blended cements.

The blended cements have a higher specific surface area (SSA) than the clinker cement. This affects the adsorption of lignosulphonate[14] and the rheological properties[16, 18]. The amount of lignosulphonate adsorbed to particle surfaces versus left in solution will change the dispersion[14]. Malhotra et al.[3] summarize the trials reported in the literature to that fly ash generally improves workability, i.e. decreases viscosity and yield point. This

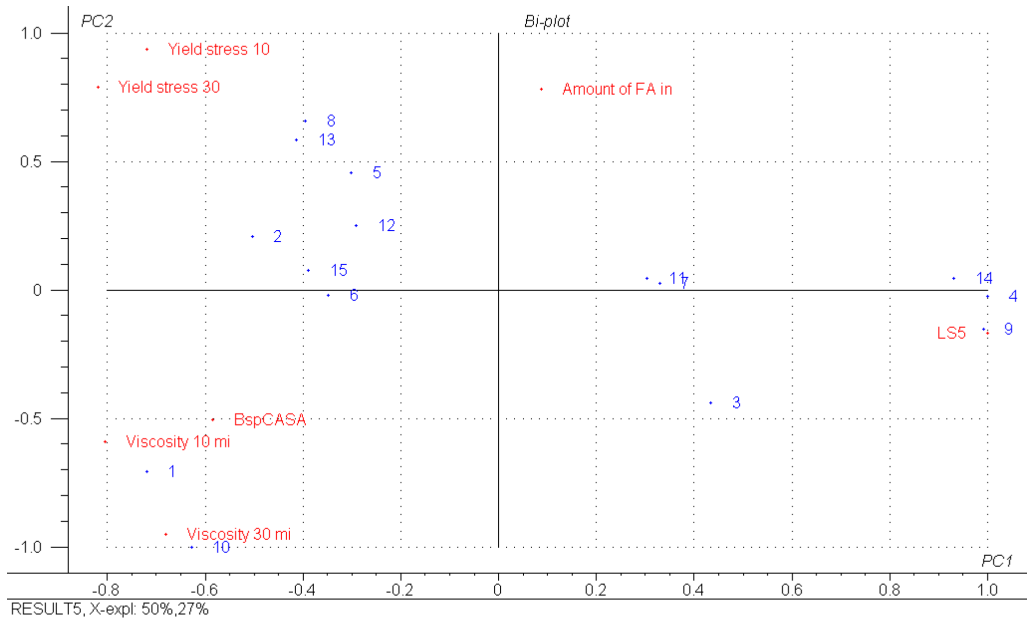

Fig. 3: Scores and loadings plot from PCA. The numbers represent each mixture and the names refer to the variables in the data set.

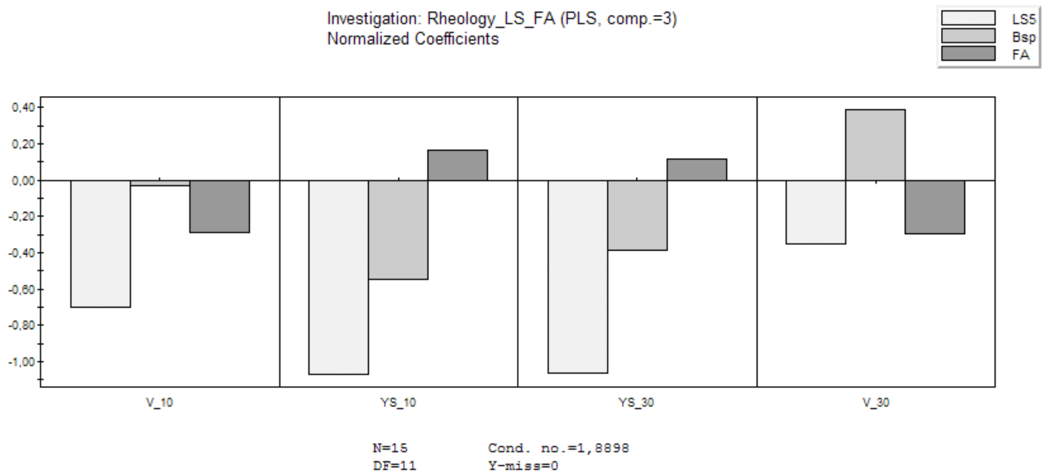

Fig. 4: Regression coefficients from PLSR for each rheological property.

effect is due to the very fine, spherical particles in fly ash.

The multivariate data analysis did not give as much information as anticipated. The reason is probably that the data set is too small for this kind of statistical analysis. More experiments needs to be added to the data set before modelling with multivariate data analysis can be fully exploited

CONCLUSION

The workability of the mortar increases with increased amount of fly ash and increased amount of lignosulphonate. To reach a certain viscosity, the amount of lignosulphonate is lower for blended cements than for cement of clinker only. This means that the blended cements need less plasticizing admixture to reach a certain water reduction than the mortar of cement consisting of clinker only.

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