

Adsorption of plasticizers – Influence of plasticizer and cement type

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ABSTRACT

Adsorption of the plasticizing agents sulfonated naphthalene formaldehyde condensate, lignosulfonate and polyacrylate was measured by UV spectroscopy and Total Organic Carbon (TOC) on five different cement slurries. The rheological properties of the slurries were measured by a parallel plate rheometer as a function of plasticizer and cement type, time and plasticizer dosage.

INTRODUCTION

The performance of superplasticizers in cementitious systems has been found to depend on cement fineness, cement composition, mode of introduction into the mixture, as well as the type and chemical composition of the superplasticizer itself^{1,2}. This paper investigates how the adsorption behaviour of the three superplasticizers sulfonated naphthalene formaldehyde condensate (SNF), lignosulfonate (LS) and polyacrylate (PA) depend upon various cement characteristics and how it affects rheological properties of cementitious pastes. The experimental work was done partly at EMPA in Switzerland and partly at SINTEF in Norway.

EXPERIMENTAL

The ultraviolet absorption spectrum of dilute aqueous solutions provides a method for the detection of aromatic and other UV-active (conjugated bonds) groups in superplasticizers. The UV spectra of

different superplasticizers (SNF, sulfonated melamine formaldehyde (SMF) and lignosulfonate) are quite different and can be used for chemical identification purposes^{1,3}. Polyacrylate-type products generally do not contain aromatic groups and do not show UV-adsorption in a readily accessible spectral region, i.e. >200 nm⁴.

The cementitious pastes were prepared from the cements 1-5 which are described in Table 1. Mixtures with SNF and LS were prepared with a w/c ratio of 0.40. The blending of the pastes was performed in a high shear mixer from Braun (MR5550CA) by adding solids to the water and mix for ½ minute, resting for 5 minutes and blending again for 1 minute. The superplasticizers were either added with the water first (immediate addition) or 5 minutes after water addition (delayed addition).

Rheological parameters were recorded 20 minutes after water addition by a parallel plate (1 mm gap, upper plate serrated to 150 µm depth) rheometer MCR 300 produced by Physica. The measurements were done isothermally at 20°C. A shear stress - shear rate curve was measured with linear sweep of shear rate from 200 down to 2 s⁻¹ in 30 points lasting 6 s each. Hysteresis, gel strength and oscillation sequences were included in the sequence, but will not be discussed further. The full measurement sequence lasted 25 minutes and was repeated 4 times to monitor time dependencies:

The pastes were filtered through 0.45 μm -filters 20 minutes after water addition. The pore solutions were diluted 50-200 times with a solution of “artificial pore water” (NaOH and KOH with a K/Na molar ratio equal to 2 and pH=13.2). The amount of superplasticizer in the water phase was read from the standard curve which had been made with a dilution series of SNF (290 nm) and LS (283 nm). The difference between the added and measured content of superplasticizer gave the bound portion.

The adsorption of PA on cement was done by measuring Total Organic Carbon (TOC) left in the pore water with a Shimadzu TOC Analyzer 5000A. Preparation of pastes and measurement of rheology was done as described above. Rheological and adsorption measurements of pastes with PA, LS and SNF were performed for comparative reasons. The cements 1-5 described by Table 1 were subjected to the investigations.

PA is a much stronger superplasticizer than SNF and LS and many cement pastes segregated even at low polyacrylate dosages when the w/c was set to 0.40. Cement pastes were therefore produced with w/c ratio in the region 0.30-0.40 in order to achieve stability. Pore water was filtrated from the pastes as described above, but this time filtrations were done every 25 minute to study time effects. The pore water was diluted 1:10 with 0.1M HCl before the TOC measurements were applied. The amount of plasticizer bound to the cement was calculated by difference between the added and the measured content of organic carbon.

Table 1: Mineral composition (%) and alkali content of Portland cements obtained by QXRD and Plasmaemissionsspectrometrie

CEMENT NO.	1	2	3	4	5
Cement Type	CEM I 42.5 RR	CEM I 42.5 R	CEM II A-V 42.5 R	CEM I 52.5 R-LA	CEM I 42.5 R-LA
Alite	64.7	66.0	60.3	65.0	61.9
Belite	14.8	9.4	7.1	12.9	19.7
Ferrite	7.5	8.7	7.1	9.6	12.0
Cubic Aluminate	5.9	3.4	3.1	0.5	0.4
Orthorhom. Aluminate	1.1	1.7	3.4	3.0	1.7
Lime	1.0	1.2	0.2	0.6	0.7
Periclase	1.6	1.2	1.7	0.3	0.4
Gypsum	0.0	0.2	0.0	1.4	1.3
Hemihydr.	1.8	2.0	2.1	1.5	0.4
Anhydrite	0.6	0.5	0.4	0.4	0.4
Calcite	0.5	4.6	0.6	4.0	0.7
Portlandite	0.3	0.4	0.5	0.3	0.2
Quartz	0.0	0.4	1.5	0.4	0.2
Arcanite	0.3	0.4	0.1	0.0	0.0
Mullite	-	-	2.6	-	-
Amorphous	-	-	9.3	-	-
Blaine	546	360	467	364	447
K (mg/l)	920	880	580	320	360
Na (mg/l)	220	170	116	74	84
Na _{eqv} (mg/l)	760	690	458	262	296

RESULTS AND DISCUSSION

Rather than describing the flow curve with the usual Bingham model, it was decided to use the area under the curve (Pa/s) as a measure of “flow resistance”. The question is whether the area under the flow curve represents something more “physical” than an “apparent” yield stress from Bingham modeling.

In a parallel plate set-up with shear area, A [m^2], and gap h [m] between the plates;

$$\tau = F/A \quad [\text{N}/\text{m}^2 \text{ or Pa}] \quad (1)$$

(average shear stress over a shear rate interval)

$$\Delta \dot{\gamma} = v/h \quad [\text{m}/\text{s} \cdot \text{m} \text{ or } \text{s}^{-1}] \quad (2)$$

(shear rate difference over an interval)

where F [N] is the force used to rotate the upper plate and v [m/s] is the velocity.

$$\begin{aligned} \text{Area under the curve} &= \tau \cdot \Delta \dot{\gamma} = (F/A) \cdot (\Delta v/h) \\ &= F \cdot \Delta v / A \cdot h = F \cdot \Delta v / V \end{aligned} \quad (3)$$

where V [m³] is the volume of the sample.

The unit of the area under the curve is then [N·m/m³·s or J/m³·s or W/m³]. It is in other words the power required to make a unit volume of the paste flow with the prescribed rate in the selected range. The power, P [W], required to mix concrete for a certain time interval is actually sometimes measured by simply monitoring voltage (U [V]) and current (I [A]) driving the electrical motor of the mixer, since $P = U \cdot I$. The flow resistance could of course have been obtained at constant shear rate, but a shear rate range of 43-8.8 s⁻¹ was used in order to compare with parameters from the Bingham model.

Graphs of consumed plasticizer and flow resistance as a function of added SNF superplasticizer are depicted in Fig. 1. The “saturation point” was defined as the superplasticizer dosage where a further addition of superplasticizers does not significantly reduce the flow resistance of the slurry.

The adsorption curve did in some cases reach a plateau value at superplasticizer saturation. Such adsorption behavior is characteristic for high-affinity adsorption in which virtually all the available polyelectrolyte binds to the adsorbent at specific surface sites until monolayer coverage is attained (i.e. Langmuir adsorption). Such a plateau was however not always easily detectable. Lower-affinity adsorption is characterized by curves in which the amount of polyelectrolyte adsorbed is always less than the polyelectrolyte dosage, with the

isotherm gradually tapering off with increasing polyelectrolyte concentration rather than attaining a definite adsorption plateau⁵.

In some cases as seen for the delayed addition of SNF to Cement 1 (Fig. 1) and immediate addition of PA to Cement 2 (Fig. 2) the adsorption decrease after reaching a maximum. This might indicate that surplus molecules in the water phase are compressing the ionic double layer or that adsorbed molecules expand and hinder molecules in the water phase to attach at the surface (osmosis). A similar phenomenon was discovered by Andersen et al.⁶ and Yoshioka et al.⁷.

Experiments with delayed addition of polyacrylate was not performed since Vikan and Justnes⁸ established that delayed addition of PA only causes marginal decrease of flow resistance. Delayed addition of SNF plasticizer to Cement 1 (Fig.1) resulted however in a strong reduction of the flow resistance and reduced amount of consumed plasticizer. The main reasons for reduced flow resistance and reduced amount of consumed superplasticizer by delayed addition have been considered to be reduced intercalation of the plasticizer in the newly formed ettringite: Since delayed addition of the polymer is not followed by a further considerable hydration of the cement (dormant period), the renewal of the surfaces active in adsorption does not occur in this case and, therefore, the amount of polymer consumed is much lower than that observed in the case of immediate addition. “Free” or available excess superplasticizers in the interstitial solution which do not intercalate or adsorb on the cement have also been found to contribute to increased flow of the paste^{9,10}.

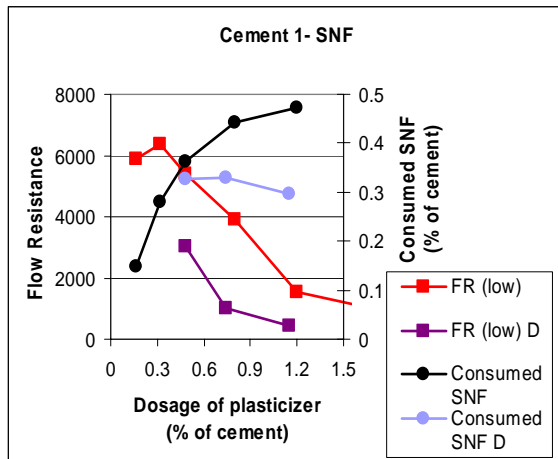


Fig. 1: Flow resistance (FR) and consumed (adsorbed and intercalated) superplasticizer as a function of plasticizer dosage for immediate and delayed addition. The plasticizer is either added first with the water or 5 minutes after water addition (D = delayed).

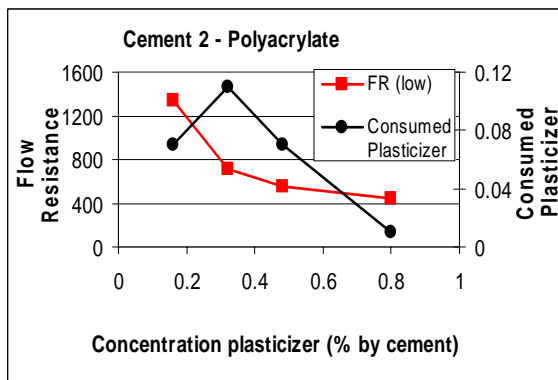


Fig. 2: Flow Resistance and amount of consumed (adsorbed and intercalated) PA as a function of added PA cement 2.

The adsorption and flow resistance measurements illustrate that PA is a much stronger plasticizer than SNF and LS since it is effective at much lower dosage. Cement 1 requires for example 1.20% SNF or 0.32% PA to obtain a flow resistance of approximately 600 W/m^3 . Similar results have been found by Golaszewski and Szwabowski¹¹ and Hanehara and Yamada¹².

It is not straight forward to analyze the adsorption data as a function of time since

the concentration of superplasticizer in the pore water might decrease by encapsulation in the hydrated cement or increase as the pore water is consumed by the hydration process. The concentration of PA, LS and SNF in the pore water did, however, not change noticeable with time. This observation is backed by Chiocchio and Paolini¹³ who claimed that the adsorption of SNF and SMF is terminated after only 1-2 minutes of mixing.

Alteration of flow resistance with time

It was generally found that flow loss is dependent on the cement type and type and dosage of superplasticizer. Flow loss generally occurred for pastes with SNF. Pastes with LS generally developed lower flow loss than pastes with SNF and flow gain was observed for several pastes. Similar results have been found by Uchikawa et al.¹⁴ who found that LS forms complex salts with Ca^{2+} more easily than SNF. Thus, the concentration of Ca^{2+} in the liquid phase, delays the saturation of Ca^{2+} , which influences the morphology of hydrate produced larger $[\text{Ca}_3(\text{Al,Fe})(\text{OH})_6]\text{X}_3 \cdot x\text{H}_2\text{O}$ (AFt) crystals are produced with LS than with SNF) and delays the setting time of cement.

Another noticeable feature for SNF is that the flow loss has a turning point at the saturation dosage where the flow loss rates increase noticeably. Nawa et al.¹⁵ found on the other hand that cement pastes with SNF and SMF superplasticizer had large flow loss rates, but the flow loss rate decreased with a higher superplasticizer dosage.

Pastes with LS tended to transform flow loss to flow gain when the added dosages reached supersaturation. Flow gain at supersaturation might indicate inhibited or reduced hydration rate due to the formation of complexes with Ca^{2+} as discussed above. Surplus LS molecules in the water phase might also adsorb onto the newly formed hydration products enabling increased flow.

Flow gain was the general trend for most pastes with PA. These results are backed up by Nawa et al.¹⁵ and Golaszewski and Szwabowski¹¹.

No turning point for flow loss as a function of PA dosage has been detected which might indicate that the grafted chains of the molecules are long enough to provide steric stabilization even if the stem is adsorbed and covered by hydration products. Table 2 shows flow loss data for Cement 2 with different dosages of the three plasticizers studied.

Table 2: Flow loss measurements for pastes of Cement 2 with SNF, LS or PA in the low shear rate range (43-8.8 s⁻¹).

Cement 1		SNF	LS	PA
SP Dose (%)	Time (min)	Flow Loss SNF(%)	Flow Loss LS(%)	Flow Loss PA(%)
0.16	20			
	45	13	7	-10
	70	21	15	-14
	95	25	19	-15
0.32	20			
	45	33	7	-7
	70	65	17	-9
	95	91	25	-11
0.48	20			
	45	64	-14	-5
	70	154	-10	-6
	95	255	-5	-7

Correlation of adsorbed plasticizer with cement characteristics

The consumed amounts of superplasticizer at saturation are given in Table 3. The table and the adsorption curves (Fig. 2) show that the saturation dosages of the superplasticizers mainly depend on the cement and to a lesser extent on the superplasticizer type when SNF and LS are considered. PA has a lower saturation than SNF and LS, but this plasticizer will not be

discussed further due to the scarce amount of data.

Ranking of the adsorption capacity of the cements seems to depend upon the superplasticizer dosage. SNF molecules adsorb somewhat stronger on cement than LS below saturation while the opposite trend is found at saturation dosage. All in all, it can be concluded that SNF and LS are adsorbed roughly at the same extent to the cements.

Table 3: Consumed (adsorbed and intercalated) superplasticizer at the point of saturation for SNF and lignosulfonate
C₃A = Ca₃Al₂O₆.

Cement	Blaine (m ² /kg)	Cubic C ₃ A (%)	Cons. LS (mg/m ²)	Cons. SNF (mg/m ²)
1	546	5.9	12.2	8.7
2	360	3.4	11.9	8.4
3	467	3.1	5.1	7.8
4	364	0.5	13.2	7.2
5	447	3.1	11.2	10.7

Cement 3 (cement with fly ash) adsorbs less superplasticizer than expected regarding its relatively high surface (Blaine) as shown in table 3. Experiments to study the influence of fly ash on the superplasticizer adsorption were therefore performed. Adsorbance of LS and SNF were measured on pastes of pure Cement 1, pure fly ash (FA), pure FA with 2% by weight Ca(OH)₂ and pastes with 50% FA and 50% Cement 1 measured by weight. The results given in Table 4 show that pure fly ash adsorbs less superplasticizer than cement, while the amount of consumed plasticizer for the cement-FA mix was found to be close to the results of pure cement. These results seem to coincide with the work of Nagataki et al.¹⁶. Pure FA pastes with 2% Ca(OH)₂ adsorbed approximately the same or slightly higher amount of plasticizer as pure cement paste. This result seems to indicate that Ca²⁺

adsorb on the FA surface and that the anionic superplasticizer molecules adsorb on the positive charged sites thus created. Jolicoeur and Simard¹⁷ pointed out a similar effect after the observation of SNF being adsorbed to a minor extent by silica fume slurry, but being equally adsorbed by cement paste and cementitious paste with silica fume replacement.

Table 4: Consumption (adsorbed and intercalated) of 1% by cement weight LS on FA and Cement 1.

Adsorbant	Consumed plasticizer (% of added)
Pure FA	24.3
50/50 Cement 1+ FA	67.4
Cement 1	69.2
Pure FA + 2% Ca(OH) ₂	69.3

Correlations of saturation dosages of SNF and LS with the cement characteristics Blaine, contents of total C₃A, cubic C₃A, soluble sodium equivalent (Na_{eqv}) and the products of some of the cement characteristics were attempted. The same procedures were not performed for pastes with PA due to the scarce amount of available data. The regression coefficients, R², in Table 5 indicate that the saturation dosage of SNF depends strongly on the single cement characteristics Blaine and content of cubic C₃A. Strong correlations were found for the saturation points with the product of Na_{eqv} and Blaine as well as the product of Na_{eqv} and cubic C₃A. The best correlation was found for the product of cubic C₃A and Blaine. This is logical since high surface and aluminate content in the cement will enforce rapid hydration which in turn leads to a high superplasticizer saturation concentration.

The saturation dosage of LS seems to have a stronger dependency on the amount of soluble alkali than observed for pastes

with SNF. This result might be caused by the fact that LS form complexes in a higher degree than SNF as discussed above. Good correlations were found between the saturation dosages with the single cement characteristics soluble sodium equivalent and cubic C₃A. A good correlation was found for the product of cC₃A with Blaine, but the best fits were found for the products Na_{eqv}·Blaine and Na_{eqv}·C₃A_{cubic}. Figure 3 shows an example of a correlation of saturation dosages of LS with the cement characteristics Na equivalent times cubic C₃A for the five cements.

Table 5: Regression coefficients for correlations of superplasticizer saturation dosage with various cement characteristics.



Cement Characteristic	R ² (SNF)	R ² (LS)
Blaine	0.8187	0.4541
C ₃ A _{tot}	0.5954	0.5372
C ₃ A _{cubic}	0.8846	0.8270
Na _{eqv}	0.5561	0.8253
C ₃ A _{tot} ·Blaine	0.7763	0.6565
C ₃ A _{cub} ·Blaine	0.9702	0.8395
Na _{eqv} ·Blaine	0.8787	0.9741
Na _{eqv} ·C ₃ A _{cub}	0.8511	0.9914
Na _{eqv} ·C ₃ A _{cub} ·Blaine	0.8805	0.9761

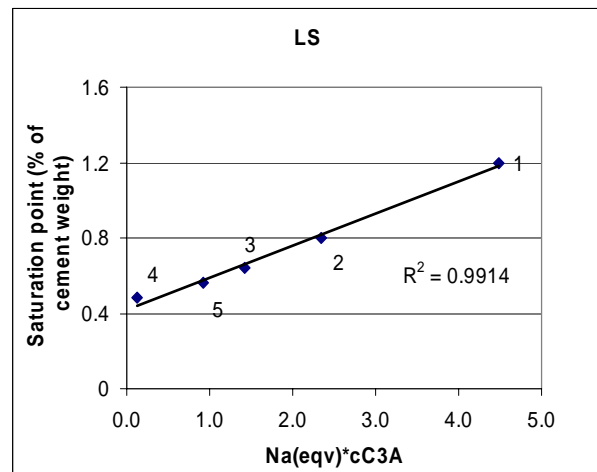


Fig. 3: Saturation point of adsorbed LS superplasticizer as a function of soluble alkalis (sodium equivalent) and cubic C₃A (Ca₃Al₂O₆). The cements are numbered according to Table 1.

In the presence of superplasticizers the influence of sulfate (easily soluble alkali sulfates) content is known to depend on the superplasticizer type. It has been found in the presence of SNF type superplasticizers that addition of alkali sulfates (Na_2SO_4) can lead to improvements in the rheological properties of cement pastes since the SO_4^{2-} ions leads to a decreased adsorption (SO_4^{2-} - superplasticizer competition) or intercalation of SNF superplasticizer in early C_3A hydrates leaving more of the latter available for paste fluidification¹⁸. The data in Table 5 seem however to indicate that increased alkali content will *increase* the saturation value of the superplasticizer indicating that more of the superplasticizer molecules are being consumed by the hydration products. It is possible of course that Na_{eqv} govern opposite effects of Blaine and cubic C_3A in a way that will bring the measuring points into a linear function and increase the correlation coefficient (R^2). This possibility is indicated in the case of LS where the correlations for the single cement characteristics Blaine and sodium equivalent give regression coefficients approximately equal to 0.8187 and 0.5561 respectively while the product of the two characteristics give a regression coefficient equal to 0.8797.

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