

**Introduction**

The modern technology makes extensive use of superplasticizers in order to improve the strength of hardened concrete by reducing the amount of water added to the fresh mix.

The phenomena associated with the fluidifying action of superplasticizers are quite complex and involve the adsorption of the macromolecules of the polymer onto the cement grains, the modification of the electrostatic charges on the surface of the cement particles and the modification of the kinetic of hydration of the various constituents of the cement.

It has been shown that, in the case of naphthalene sulfonate condensates, there is a relationship between the effectiveness as superplasticizer and the degree of polymerization, expressed by viscosity measurements (1).

Gel Permeation Chromatography (GPC) has been used by various authors to determine the molecular weight of superplasticizers based on condensates of naphthalene sulfonic acids with formaldehyde (2,3,4).

Recently, the influence of the molecular weight of naphthalene based polymers on the rheological properties of mixes made with different cements has been studied. It has been shown that the fluidity of the mixes increases up to a maximum value, which occurs at different values of the molecular weight of the polymer, depending on the cement used. Moreover, with polymers having extremely high values of molecular weight, a decrease in the fluidity of cement mixes has been observed (5).

In the present work, GPC and ultrafiltration have been used to study the effect of the degree of condensation of polymers based on naphthalene sulfonate on the fluidity of cement pastes, in a range for which an increase of the molecular weight of the condensate causes an increase in the fluidity of the cement mixes. In particular, the purpose of the present work is to examine whether the increase in the effectiveness of the superplasticizer with its degree of condensation is due either to the reduction in the low molecular weight fraction or to the change in the molecular weight distribution of the highly condensed polymeric fraction.

**Experimental**

**Materials**

**Synthesis of naphthalene sulfonate based superplasticizer**

Pure naphthalene (10.00 kg) was charged in a glass reactor and heated at 120°C. Then 9.36 kg of 98% H<sub>2</sub>SO<sub>4</sub> (H<sub>2</sub>SO<sub>4</sub>/C<sub>10</sub>H<sub>8</sub> molar ratio = 1.07) were added and the temperature was raised at 165°C. This temperature was maintained for two hours to complete the sulfonation of naphthalene. The sulfonation mixture was diluted with 5.97 kg of water and then 7.81 kg of 36% formaldehyde solution (HCHO/C<sub>10</sub>H<sub>8</sub> molar ratio = 1.20) were added. The condensation was carried out at 112°C for 14 hours and 7 samples of polymer were collected (one every 2 hours) having increasing degree of condensation. The samples, after neutralization with sodium hydroxide, had a total solids content of about 40% by weight.

**Cement**

Type I Portland cement with Blaine fineness of about 0.4 m<sup>2</sup>/g has been used. The chemical composition of the cement is shown in Table 1.

Table 1. Chemical analysis of the cement used

CONSTITUENT	PERCENTAGE
SiO <sub>2</sub>	21.56
Al <sub>2</sub> O <sub>3</sub>	4.88
Fe <sub>2</sub> O <sub>3</sub>	2.30
CaO	60.64
MgO	2.15
K <sub>2</sub> O	0.66
Na <sub>2</sub> O	0.39
SO <sub>3</sub>	3.37
LOSS ON IGNITION	3.87

**Techniques**

**Gel Permeation Chromatography**

The samples of naphthalene sulfonic acid formaldehyde condensate to be analyzed were dissolved in 0.55 M KNO<sub>3</sub> aqueous solution to obtain concentrations of 3.0 g/100 ml.

The samples were analyzed using 0.55 M KNO<sub>3</sub> aqueous solution as eluant at a flow rate of 1 ml/min.

Shodex Ionpak S-803/S (exclusion limit 50,000 dalton) and Shodex Ionpak S-804/S (exclusion limit 500,000 dalton) coupled columns, made by semirigid crosslinked styrene-divinylbenzene sulfonate gel, were employed.

Columns were kept in a thermostatic oven at 48°C and all the samples were analyzed at this temperature.

Samples of monodisperse polystyrene sulfonate of different molecular weights (4,400-6,500-17,400-39,900-104,000), naphthalene 2-sulfonate and naphthalene 1,5-disulfonate were used as calibration standards for the columns.

Analyses were performed with a Perkin-Elmer liquid chromatograph equipped with pump mod. Series 4 and Perkin-Elmer ultraviolet detector mod. LC75 at a wavelength of 292 nm.

Chromatographic data were collected and processed by a Perkin-Elmer Data Station mod. 1600 equipped with Chromatographics 2 and GPC4 programs, both by Perkin-Elmer, used for data collection and data processing, respectively.

**Ultrafiltration**

Samples withdrawn after 4 and 14 hours of condensation were ultrafiltered in order to remove the monomer and the lower molecular weight products. Amicon stirred cell mod. 8200 and Amicon ultrafiltration membranes mod. YH2 having a nominal cut-off of 1,000 dalton, were employed.

**Mini-slug test**

The fluidity of fresh cement pastes (water/cement ratio = 0.35) in the presence

of the condensates (0.4% of dry product by weight of cement) was evaluated by the mini-slug test, after five minutes of mixing. The results were expressed in cm by measuring the area of the circular path described by the fresh cement paste, after having picked-up the cone (6).

**Results and Discussion**

In Fig. 1 the progressive development of the condensation reaction is shown, as it results from the GPC analyses at different condensation times.

According to the GPC theory, the higher molecular weight fractions elute at first, followed by the lower molecular weight fractions and the monomer (naphthalene 2-sulfonate). From Fig. 1 it is possible to recognize that, by increasing the condensation time, the monomer and the lower molecular weight fractions decrease and conversely the higher molecular weight fractions increase.

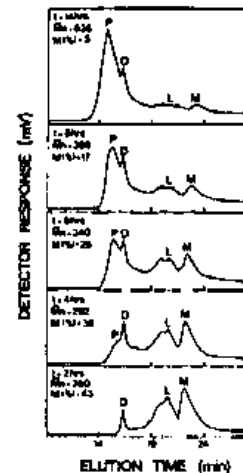


Fig.1 GPC chromatograms of some condensation products at different times (h) of reaction and different number average molecular weight ( $\bar{M}_n$ ). P = Polymer; M = Monomer; L = Low molecular weight fraction; D = Naphthalene disulfonate.

Fig. 2 shows the fluidity of fresh cement pastes as a function of the monomer content in the superplasticizer. It can be seen that there is a strong negative influence of the monomer content in the superplasticizer on the fluidity of cement pastes. This agrees with the results of authors who found that naphthalene 2-sulfonate does not exert any fluidifying effect (7).

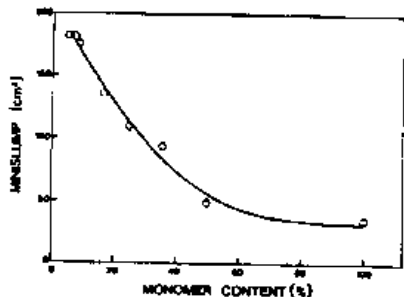


Fig. 2 Effect of monomer content in the condensation product on the fluidity (mini-slump) of the cement pastes.

In Fig. 3 the mini-slump values are plotted versus the number average molecular weight ( $\bar{M}_n$ ) of the condensate. This figure shows that, with the cement used in the present work, the fluidity increases by increasing the  $\bar{M}_n$  value up to about 500.

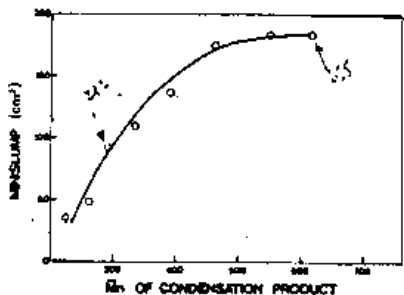


Fig. 3 Effect of  $\bar{M}_n$  of the condensation product on the fluidity (mini-slump) of the cement pastes.

By comparing the sample condensed for 4 hours ( $\bar{M}_n = 292$ ) with that condensed for 14 hours ( $\bar{M}_n = 535$ ), the latter appears to be much more effective as superplasticizer (Fig. 1). One cannot know whether the 14hr-condensate sample is better for the lower content in monomer and "L" fraction or for the higher molecular weight of the "P" fraction (Fig. 1). To clarify this point, both the samples were subjected to ultrafiltration process in order to remove the monomer and the "L" fraction. Figure 4 shows the GPC chromatograms of the two samples before and after ultrafiltration process. The mini-slump values of the cement pastes treated with condensation products before and after the ultrafiltration are shown in Table 2. The results show that, although the ultrafiltered products have different  $\bar{M}_n$  values, their fluidifying effect is substantially the same. This demonstrates that, at least for the range of molecular weights considered in the present work, the "P" fraction content and not its molecular weight is determining the fluidifying effect of naphthalene based condensates.

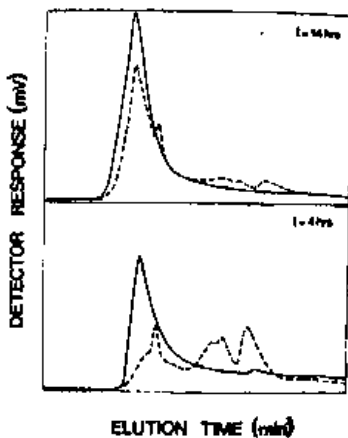


Fig. 4 GPC chromatograms of superplasticizer samples condensed for 4 hrs and 14 hrs before (dotted line) and after ultrafiltration.

Table 2 Effect of ultrafiltration on  $\bar{M}_n$  and mini-slump.

ULTRAFILTRATION	BEFORE	CONDENSATION TIME	$\bar{M}_n$	MINI-SLUMP (cm)
		4 HOURS	14 HOURS	292
			435	185
AFTER	4 HOURS		435	185
ULTRAFILTRATION	14 HOURS		735	185

Conclusions

It is possible to conclude that, for the range of  $\bar{M}_n$  of the condensate examined in the present work, the effectiveness of Naphthalene sulfonate polymer as superplasticizer is in relation to the content of the monomer and the lower molecular weight fraction, while the molecular weight value of the highly condensed polymeric fraction of the condensate is not determining the effectiveness of the superplasticizer. By using different cements, or by varying the range of  $\bar{M}_n$  of the polymer examined, different results may be obtained, as previously reported (5).

References

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