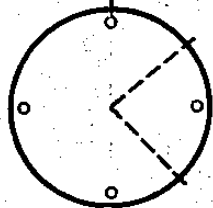


Developments in the Use of Super- plasticizers



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Influence of Polymerization of Sulfonated Naphthalene Condensate and its Interaction with Cement

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Synopsis : More than twenty naphthalene sulphonated formaldehyde condensates have been synthesized with various degrees of polymerization. This was evaluated by viscosity measurements of the polymer in water solution. Polymer adsorption, zeta potential, fluidity and compressive strength of cement mixtures have been examined as a function of the degree of polymerization and the polymer dosage. Polymer adsorption, zeta potential and fluidity increase by increasing the polymer dosage in the range of 0.25 - 2.00 % by weight of cement. Polymer adsorption, zeta potential, fluidity increase by increasing the degree of polymerization. However, above a certain degree of polymerization all the above mentioned properties do not change further. Cement particles adsorb the polymer molecules and this causes an increase in the electrical charge on the cement surface. This results in a better dispersion of cement particles and a more fluid system. However, even if there is a certain interaction between fluidity and zeta potential, the latter is not the only parameter controlling the fluidity of the system. At the same water/cement ratio, by increasing the degree of polymerization the strength is, in general, slightly increased and this seems to be related to a better dispersion of cement particles.

Keywords: adsorption; cement pastes; cements; chemical analysis; compressive strength; mortars (material); naphthalene compounds; physical properties; plasticizers; polymerization; viscosity; water-cement ratio; workability; zeta potential.

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INTRODUCTION

Superplasticizers are essentially based on sulphonated naphthalene-formaldehyde polymers or sulphonated melamine-formaldehyde polymers (1). A large amount of work has been devoted to examine the properties of fresh and hardened concrete containing commercial superplasticizers (2). However, relatively few papers have been published to study the effect of superplasticizers on the water-cement system. In particular, few papers (3-5) have appeared on the effect of pure chemical products (used as superplasticizers) on the physical-chemical changes of cement pastes. In a previous paper (5) the influence of the sulphonated naphthalene monomer and the sulphonated naphthalene formaldehyde condensed polymer on the physical-chemical properties of a cement paste was studied.

This investigation pertains to a study of the interaction between pure sulphonated naphthalene formaldehyde condensed polymer and cement. Twenty eight different polymers were synthesized and fluidity, polymer adsorption, zeta-potential and compressive strength properties were studied.

EXPERIMENTAL

Materials

The polymers were synthesized at 115°C in a laboratory pilot plant using reagent grade naphthalene sulphonic acid and formaldehyde in the molar ratio of 1. Different degrees of polymerization or different average molecular weights were obtained by changing the reaction time. It is assumed that an increase in the average molecular weight of the polymer causes an increase in the viscosity of a 28 % polymer water solution. Solution viscosity is basically a measure of the size or extension in space of polymer molecules (6). The viscosity of the 28 % acid solution was measured by a Cannon-Fenske viscosimeter at 20°C. The 28 % concentration was chosen to enable measuring different viscosities without changing the viscosimetric equipment. A higher concentration, such as 42 % corresponding to the water solution obtained in the industrial process would have required different viscosimetric techniques.

After viscosity measurements, the 28 % naphthalene sulphonic acid formaldehyde polymer solutions were neutralized with sodium hydroxide to obtain pH 9

A Type I Portland cement was used for paste and mortar tests. Table I shows the chemical composition of the cement.

A natural sand with a maximum size of 5 mm was used to prepare mortar specimens.

Procedure and test methods

The following measurements were carried out at 20°C: fluidity, polymer adsorption, zeta potential for cement pastes and compressive strength for mortars.

The neutralized polymer solutions were added to the mixing water of paste or mortar specimens so that the dry polymer content was 0.25, 0.50, 1.0 and 2.0 % by weight of cement. In general, for making superplasticized concretes the dry polymer content by weight of cement was between 0.30 and 0.50 %

Fluidity

Cement paste fluidity was measured with a "mini-slump" test technique (7) in which fluidity is related to the area (cm²) attained by a pat of cement paste on its release from a miniature

slump cone. Pastes were prepared by adding the 28 % neutralized polymer solution and water and mixing for 1 min. The solution/cement ratio was 0.4.

Adsorption

The measure of surface adsorption of the polymers on the cement was determined by U.V. absorption spectroscopy in the 220-230 mm absorption band. Cement (100 g), water and polymer solution were mixed for 5 mins. The solution/cement ratio was 2. The liquid phase was separated by vacuum filtration and was diluted to the optimum concentration. The pH was adjusted at 6.5 before spectroscopic measurement. The percentage of polymer adsorbed by cement was calculated by the difference in concentrations of polymer in the aqueous phase before and after adsorption.

Zeta potential

Zeta potential measurements were performed using a Laser Zee Meter manufactured by Pen Kem Inc. which is based on electrophoretic technique (8) and gives the results directly in millivolts. Zeta potential of colloidal particles is measured by determining the rate at which these particles move in a known electric field. Zeta potential measurements were performed with a solution/cement ratio of 2. The samples for the measurements were prepared by mixing continuously 100 g of cement, 200 g of water and a certain amount of polymer, then separating the liquid phase by vacuum filtration. Small portions of the solid were added to the filtered liquid phase and a suspension (10 mg of solid per 20 ml of liquid) was obtained with the same ionic strength of the original paste and diluted enough in order to be observed by the microscope of the Laser Zee Meter.

Strength

The compressive strength of mortar cubes (100 mm) was obtained on specimens, cured from 1 day to 28 days, at a water/cement ratio of 0.4, a sand/cement ratio of 3 and containing different amounts of dry polymer ranging from 0.25 % to 2.00 % by weight of cement.

DISCUSSION OF RESULTS

In Fig. 1 the mini-slump of cement pastes containing 0.50 % of dry polymer as a function of the polymer solution viscosity is shown. The polymer with the lowest degree of polymerization corresponding to a solution viscosity of 3.5 centistokes gives a

mini-slump of 50 cm², whereas the plain cement paste without polymer gives a mini-slump of 40 cm². By increasing the polymer solution viscosity from 3.5 to 6 centistokes the fluidity of the paste is greatly increased so that the mini-slump goes from 50 to about 125 cm². A further increase in the molecular weight of the polymer, therefore in terms of the solution viscosity from 6 to a maximum of 26.2 centistokes causes only an insignificant change in the mini-slump values.

Similar results were obtained by using the other dosages of polymer (0.25 - 1 - 2%), the only difference being that the higher the polymer amount, the higher the maximum value of slump.

In Fig. 2, the percentage of polymer adsorbed by the cement as a function of the polymer solution viscosity is shown. By increasing the polymer solution viscosity from 3.5 to about 6 centistokes there is an increase in the percentage of adsorbed polymer from about 60 to about 83 %. A further increase in solution viscosity from 6 to 26.2 centistokes rises the percentage of adsorption to only 85 %. So, it seems that an increase in the average molecular weight over a certain value - roughly corresponding to a 28 % polymer solution viscosity of 6 centistokes - causes only an insignificant change in fluidity (Fig. 2) and in polymer adsorption (Fig. 3). The data of Fig. 2 refer to the cement paste containing 0.50 % of dry polymer by weight of cement. Similar results were obtained with the other dosages of polymer, except that the maximum amount of polymer adsorbed on cement increased by rising the polymer dosage from 0.25 to 2.00 %.

In Fig. 3 the influence of the 28 % polymer solution viscosity on the zeta potential is shown.

The zeta potential of the water-cement system without polymer is about -8 millivolts.

In the presence of 0.50 % of polymer there is a strong increase in zeta potential up to -23.5 millivolts by increasing the polymer solution viscosity to 6 centistokes. No further substantial change is observed when the average molecular weight of the polymer is increased. Similar results are obtained with different polymer dosages. However, the maximum value in the zeta potential increases by increasing the polymer dosage from 0.25 % to 2.00 % by weight of cement.

In Fig. 4 mortar compressive strengths at 1, 7 and 28 days in the presence of 0.50 % of polymer are shown as a function of

the polymer solution viscosity. All the specimens containing the polymer have mortar compressive strengths higher than the corresponding mixes without polymer. As the water/cement ratio was the same (0.40) for superplasticized and plain mortars, it seems that the polymer increases strength. This benefit increases by increasing the polymer molecular weight up to a certain value corresponding to a polymer solution viscosity of about 6 centistokes. Further increases in the molecular weight of the polymer and then in its solution viscosity do not cause any significant change in the compressive strength.

Similar results were obtained with the other polymer dosages. However, when 2 % of the polymer was used, superplasticized mortars showed, at 1 day, lower compressive strengths than the mixture without polymer. So, with 2 % of the polymer there is a retarding effect at early curing and this effect is more remarkable with a higher molecular weight of the polymer (5). This is illustrated in Fig. 5 where the influence of the polymer dosage on the compressive strength of mortars at 1 and 28 days is shown. The full curves refer to polymers with a higher molecular weight (polymer solution viscosity ≥ 7 centistokes) and the dashed ones refer to polymers with a lower molecular weight (polymer solution viscosity = 3.5 centistokes).

In order to explain the effect of the polymer on the mortar compressive strength at the same water/cement ratio the following mechanism is proposed. The polymer is adsorbed on cement particles and the adsorption increases by increasing the molecular weight of the polymer. Also the zeta potential becomes higher by increasing the polymer molecular weight. Increases in both adsorption and zeta potential cause a better dispersion of cement particles and a more homogeneous microstructure of the cement paste. According to Verbeck (9) a homogeneous microstructure gives a higher strength than a heterogeneous one. On the other hand, this beneficial effect is counterbalanced by the retardation in cement hydration at early ages caused by polymer adsorption on cement particles. Therefore, when the polymer dosage is increased over a certain value (for instance 1 % in Fig. 5), there is no further improvement in cement dispersion, the compressive strength is reduced because of the stronger retardation at early ages. This effect is of course more pronounced at 1 day than at 28 days (Fig. 5). On the other hand, as the high viscosity (≥ 7 centistokes) polymer is adsorbed on cement particles to a greater extent than the low viscosity (3.5 centistokes) polymer (Fig. 2), the retardation of cement hydration is more remarkable when a high viscosity polymer is used (Fig. 5).

According to Roy (4) attractive forces exist among cement particles in cement pastes, and, in time, particles link together to build rigid networks. Superplasticizers are assumed to be effective in breaking the cement particle networks and dispersing them, preventing premature linkage and minimizing the amount of water required to disperse the particles and render the mixture workable. High values in zeta potential and electrostatic repulsive forces cause dispersion of colloidal particles (8). In Fig. 6 the influence of zeta potential on fluidity of cement paste is shown for high and low viscosity polymers. The figures on the curves indicate the percentages of polymer addition by weight of cement. The higher the zeta potential the more fluid the cement paste. However, the relationship between fluidity and zeta potential depends on the type of polymer, as for example for the same zeta potential the mini-slump is much higher when the high viscosity polymer is used. Therefore, even if the zeta potential affects the mini-slump, it is not the only parameter controlling the fluidity of cement mixtures.

In Fig. 7 the influence of polymer adsorbed by weight of cement on the fluidity of the cement paste is shown. The figures in the curve indicate the percentage of polymer addition by weight of cement. The higher the polymer adsorption, the higher the mini-slump, and a remarkable increase in fluidity is achieved by increasing the percentage of polymer adsorbed on cement from 0.3 to 0.8%. Only one curve seems to be required to correlate the mini-slump and the polymer adsorption independently of the polymer viscosity. The polymer adsorption on cement particles is possibly more important than the zeta potential in determining fluidity. However, in order to obtain the same percentage of polymer adsorption, and the same fluidity, a higher amount of low viscosity polymer is required (Fig. 7). For example, to adsorb 0.43 % of polymer on cement particles and then to obtain the same mini-slump (about 115 cm²) 0.5 % and 1 % of polymer are required for the high viscosity and the low viscosity polymer respectively (Fig. 7). On the other hand, with these percentages of polymer addition the zeta potential is -24 millivolts and -36 millivolts for the high viscosity and the low viscosity polymer respectively, although the same mini-slump (about 115 cm²) was obtained. This would indicate that the dispersion of cement particles by superplasticizers is determined not only by an increased zeta potential but also by steric hindrance of polymers adsorbed on cement particles (10).

CONCLUSIONS

The degree of polymerization of naphthalene sulphonated formaldehyde condensates used as superplasticizers influences the fluidity of cement mixtures. Polymers having high molecular weight, corresponding to a 28 % solution viscosity of at least 7 centistokes, are more effective than low molecular weight polymers (viscosity = 3.5 centistokes) in increasing fluidity of cement pastes. This seems to be related to an increase in both zeta potential and polymer adsorption causing steric hindrance. Mortar compressive strength is also increased by increasing the degree of polymerization of the condensate except at early ages (1 day) when high dosages of superplasticizer such as 2 % of dry polymer by weight of cement are used.

REFERENCES

1. Joint Working Party, "Superplasticizers in Concrete", Cement Admixtures Assn. & Concr. Assn., Cem. Concr. Assn., Wexham Springs, UK, 1976.
2. Proceedings of an International Symposium "Superplasticizers in Concrete", Ottawa, 1978.
3. Kondo, R., Daimon, M., Sakai, E., "Interaction between Cement and Organic Polyelectrolytes", *Il Cemento*, V.75, No.3, July 1978, pp. 225-230.
4. Roy, D.M. et al, "Rheological Properties of Cement Mixes", *Cem. Concr. Res.*, V.8, No.5, Sept. 1978, pp.753-764, V.9, No.1, Jan. 1979, pp.103-110, V.9, No.6, Nov. 1979, pp. 731-740, V.10, No.2, March 1980, pp. 287-295.
5. Collepari, M., Corradi, M., Baldini, G., Pauri, M., "Influence of Sulfonated Naphthalene on the Fluidity of Cement Pastes", Proceedings, V. III, 7th International Congress on the Chemistry of Cement, Paris, 1980, pp. VI.20-25.
6. Billmeyer, F.W. Jr., "Textbook of Polymer Science", Interscience Publishers, New York, 1966.
7. Perenchio, W.F., Whiting, D.A. and Kantro, D.L., "Water Reduction, Slump Loss and Entrained Air-Void Systems as Influenced by Superplasticizers", ACI SP-62, "Superplasticizers in Concrete", 1979, pp. 137-156.

8. Riddick, T.M., "Control of Colloid Stability through Zeta Potential", Zeta Meter Inc., New York 1968, 372 pp.
9. Verbeck, G., "Cement Hydration Reactions at early Ages", Res. Dept. Bull., Portland Cement Assn., Skokie, USA, 1965, 189 pp.
10. Kreijer, P.C., "Plasticizers and dispersing Admixtures", Proceedings, V. Admixtures, Concrete International 80 Conference, London, 1980, pp. 1-16.

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Table I

Chemical analysis of the Portland cement

OXIDE	COMPOSITION	COMPOUND	COMPOSITION
CaO	63.6 %	C ₃ S	= 57 %
SiO ₂	20.8 %	C ₂ S	= 19 %
Al ₂ O ₃	5.5 %	C ₃ A	= 10 %
Fe ₂ O ₃	3.0 %	C ₄ AF	= 10 %
MgO	0.8 %		
Na ₂ O	0.2 %		
K ₂ O	0.4 %		
SO ₃	2.9 %		
Loss on ignition 2.0 %			
Insoluble residue 0.2 %			
Blaine fineness 385 m ² /kg			

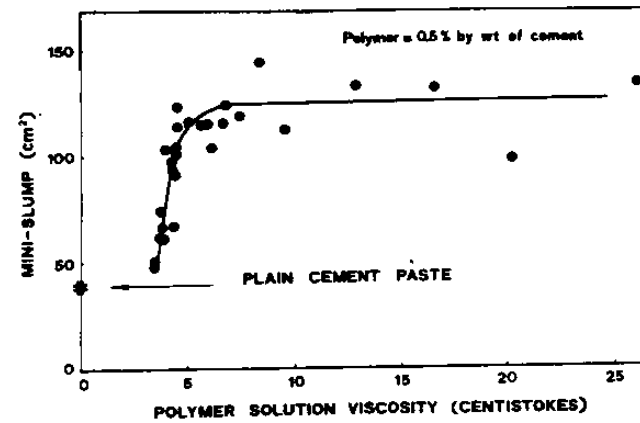


Fig. 1--Influence of polymer solution viscosity on cement paste mini-slump

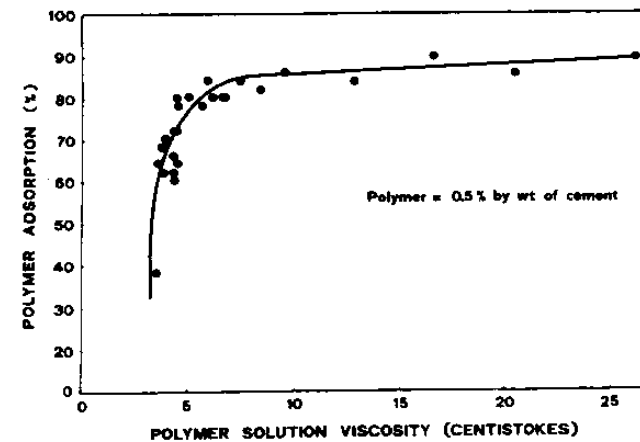


Fig. 2--Influence of polymer solution viscosity on the percentage of polymer adsorbed by cement

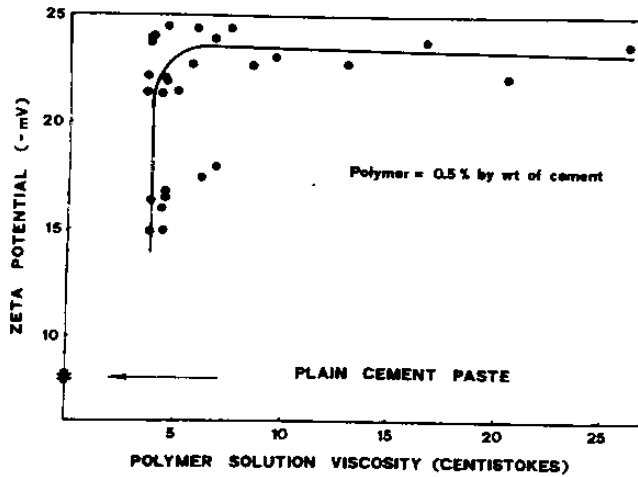


Fig. 3--Influence of polymer solution viscosity on zeta potential

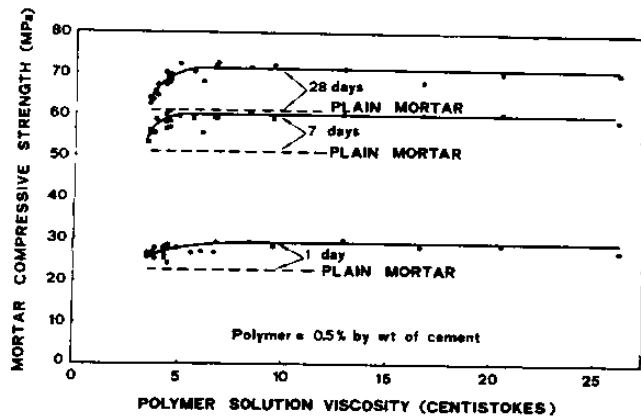


Fig. 4--Influence of polymer solution viscosity on mortar compressive strength

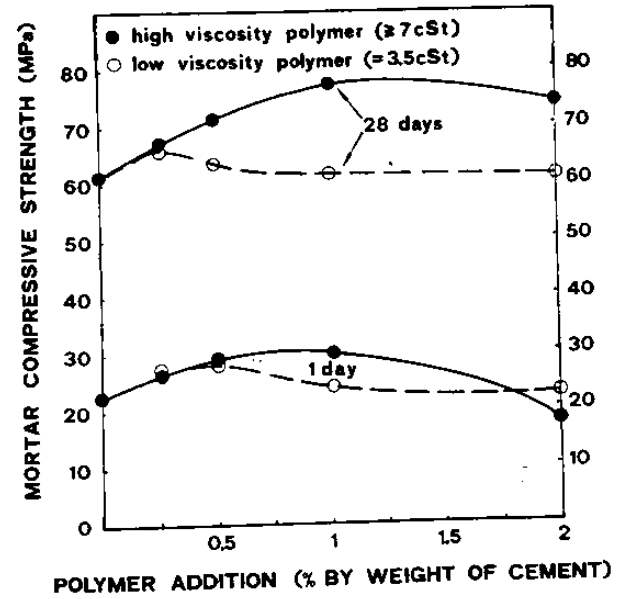


Fig. 5--Influence of polymer percentage on mortar compressive strength

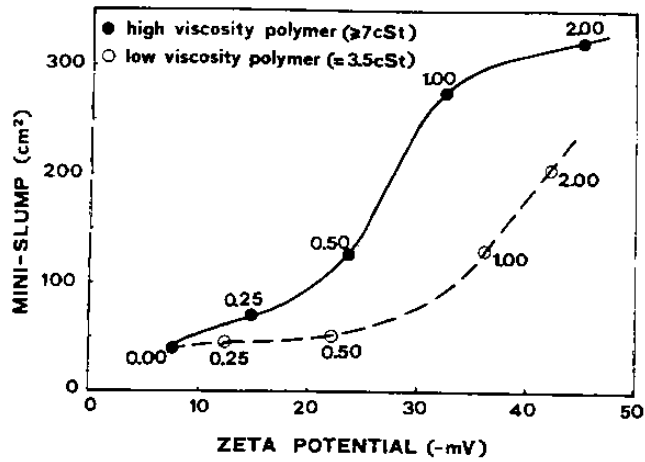


Fig. 6--Influence of zeta potential on mini-slump of cement paste. The figures on the curves indicate the percentage of polymer addition by weight of cement

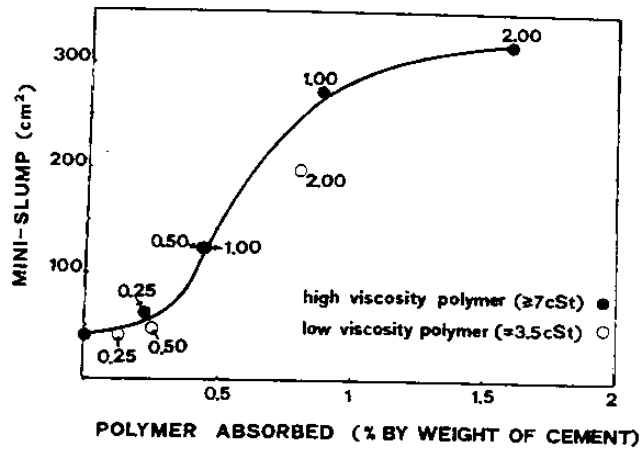


Fig. 7--Influence of percentage of polymer adsorbed on mini-slump of cement paste. The figures on the curve indicate the percentage of polymer addition by weight of cement