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PROPERTIES OF CEMENT MIXES CONTAINING NAPHTHALENE SULFONATED POLYMERS OF DIFFERENT MOLECULAR WEIGHT

Introduction

Sulfonated Naphthalene-formaldehyde polymers are the basic materials for the production of a class of superplasticizers, which are today extensively used to manufacture cement concretes and mortars. While a large amount of work has been devoted to examine the properties of fresh and hardened concretes containing superplasticizers (1,2), relatively few papers have been published to examine the effect of superplasticizers on the chemical characteristics of polymers and cement mixes (3-6).

This investigation was therefore carried out in order to correlate performances of cement mixes (including mortars), with the physico-chemical characteristics of cement pastes, manufactured with and without the addition of Naphtalene based superplasticizers.

In particular the work was carried out with a series of different superplasticizers based on sulfonated Naphthalene, in order to evaluate the effect of the polymer molecular weight on the hydration of cement and the performances of cement mixes.

Experimental

Materials

Four samples of sulfonated Naphthalene polymers of different molecular weight were obtained by a process described in an other work (7), where the final condensation step was maintained for 2, 4, 10 and 14 hrs respectively, at a temperature of 112°C.

The Number Average Molecular Weight ($\overline{Mn}$) of condensated superplasticizers was determined by use of Gel Permeation Chromatography (8) and specific values for each sample of polymer are given in Table 1.

Table 1 Number Average Molecular Weight ($\overline{Mn}$) of different samples of condensated Naphthalene sulfonate.

SAMPLE	CONDENSATION TIME (hrs)	$\overline{Mn}$
A	2	260
B	4	290
C	10	480
D	14	640

A type I ASTM Portland cement was used, and its chemical analysis is given in Table 2.

Table 2 Chemical analysis of Portland cement

	%w
L.O.I.	1.20
SiO_2	21.05
Al_2O_3	5.20
Fe_2O_3	3.12
CaO	63.70
MgO	0.75
Na_2O	0.20
K_2O	0.37
SO_3	1.90
Blaine fineness (m^2/gr)	0.380

Techniques

Polymer adsorption, zeta potential, minislump, heat evolution rate, differential thermogravimetry (DTG) were carried out on cement pastes (water/cement ratio = 0.40) hydrated at 20°C by following the techniques described in previous papers (5,6). Polymer adsorption, zeta potential and minislump were determined after 5 min of mixing. Moreover ASTM (with only 5 days) flow table, air-entrainment measurement and compressive strength on mortar mixes at 20°C (sand/cement ratio = 3) were carried out at a given water/cement ratio (0.45) or at a given flowability (flow cone = 70%).

The superplasticizer dosage was 0.4% of dry polymer by weight of cement.

Discussion of results

Fig.1 shows the polymer adsorbed on cement (by percentage of the original amount of polymer) as a function of its Number Molecular Weight ($\overline{Mn}$). By increasing $\overline{Mn}$ the polymer adsorption increases up to 70%. Beyond an $\overline{Mn}$ value of about 600 it seems that there is no significant increase in the polymer adsorption.

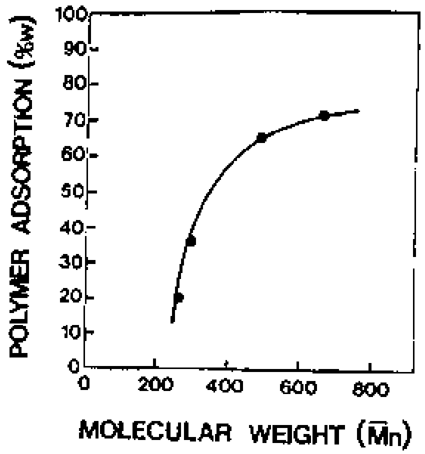

Fig.1 Adsorption of Naphthalene sulfonate polymers on cement paste as a function of the Number Molecular Weight (M̄n) of polymers.

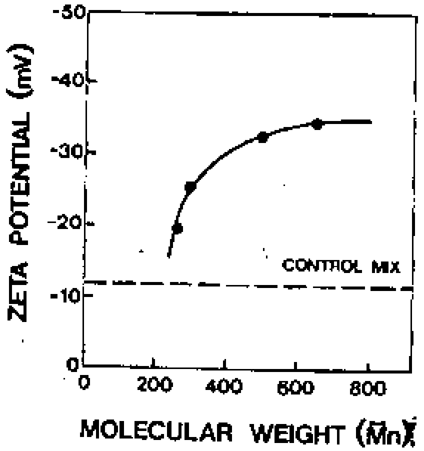

Fig.2 Zeta potential of cement pastes with and without Naphthalene polymers of different Molecular Weight (M̄n).

A similar trend was recorded for the zeta potential vs M̄n curve (fig. 2). Also in this case it seems that there is no substantial increase in zeta potential for M̄n values higher than 600.

Figure 3 shows that the fluidifying effect of the polymer increases by increasing the polymer M̄w value. Also in this case it seems that the effect does not substantially change with polymers having M̄n value higher than about 600.

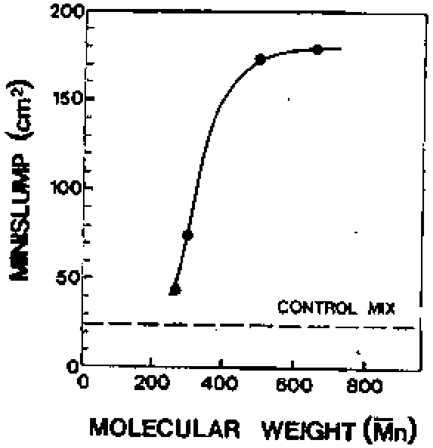

Fig.3 Minislump of cement pastes prepared with and without addition of Naphthalene polymers of different Molecular Weight (M̄n).

Curves of heat evolution rate as a function of hydration time up to 24 hrs with and without superplasticizers are shown in Fig. 4. In the presence of those admixtures both the induction period and the time corresponding to the maximum in the heat evolution curve are increased with respect to the control mix without admixture. This indicates a retarding effect of the polymer on the early cement hydration. The higher the polymer M̄n value, the more effective the retarding action of the polymer.

In order to obtain more information about the effect of the polymer on the cement hydration, the percentage of $Ca(OH)_2$ produced from 8 hrs to 28 days was

determined by DTG (Table 3). At 8 hrs the percentage of $Ca(OH)_2$ decreases in the presence of polymers with respect of control mix. The higher the polymer M̄n value, the more effective is the retarding action on the early cement hydration, thus confirming the results obtained by the calorimetry technique (Fig. 4). On the other hand, at longer ages, such as 7 and 28 days, the polymer addition increases the cement hydration degree and the effect becomes more remarkable by increasing the molecular weight of the polymer.

Table 3 $Ca(OH)_2$ (% by weight of anhydrous cement) in pastes cured with and without Naphthalene polymers of different Molecular Weight (M̄n)

MOLECULAR WEIGHT OF POLYMER (M̄n)	$Ca(OH)_2$ (%w) after:			
	8 hrs	1day	7days	28days
CONTROL	2.0	7.3	9.0	10.5
260	1.8	6.6	9.5	10.7
290	1.7	6.5	10.5	11.2
480	1.6	6.7	11.0	12.1
640	1.5	6.8	12.0	15.2

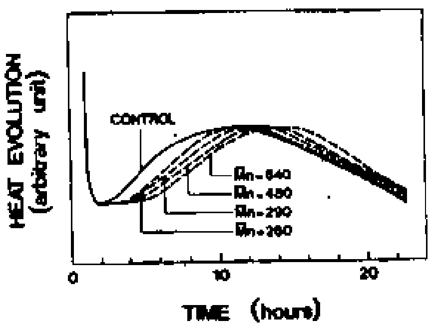

Fig.4 Heat evolution curves of cement pastes with and without addition of naphthalene sulfonate polymers of different Molecular Weight (M̄n).

Table 4 and 5 show the results on mortars at a given w/c ratio and at a given flowability respectively. For the tests at a given w/c ratio, the superplasticizer addition causes an increase in the flow table of the mortar. The fluidifying effect increases by increasing the polymer M̄n value. On the other hand the polymer addition causes an increase in the air-entrainment. This effect is greatest with the polymer having M̄n value of 290. It would seem that the air-entrainment decreases with the molecular weight of the polymer and increases with the fluidity of the mortar, so that the highest increase in the air-entrainment is caused by the polymer with an intermediate M̄n value such as 290 in the present work. Because of the high increase in the air-entrainment, the strengths of mortars with polymers having M̄n values of 260 and 290 are lower than the strength of the plain mortar, in spite of a higher cement hydration degree at 7 and 28 days of the superplasticized cement mixes with respect to the control mix (Table 3). For the polymers with M̄n of 480 and 640 causing a lower increase in the air-entrainment, the strength of the superplasticized mortars at later ages (7 and 28 days) are slightly higher than the control mortar.

Table 4 Characteristics of mortars (water/cement = 0,45; sand/cement = 3) prepared with and without Naphthalene sulfonate polymers of different Molecular Weight (M̄n).

M̄n OF POLYMER	FLOW *	ENTRAINED AIR	COMPRESSIVE STRENGTH (MPa)		
		%v	1day	7days	28days
CONTROL	65	5.0	13.5	42.0	52.5
260	80	9.0	12.5	37.0	47.5
290	90	12.0	10.5	33.0	44.0
480	110	8.5	12.0	43.0	53.0
640	130	7.5	13.0	44.0	55.5

* ASTM C 109 – 5 drops only

The effect of the polymer $\bar{M}n$ value on the air-entrainment in superplasticized mortars appears clearer in the tests at a given flowability (Table 5). In this case the increase in the air volume caused by the superplasticizer decreases by increasing the polymer $\bar{M}n$ value from 280 to 640. The increase in strength is remarkable with the polymers having the highest $\bar{M}n$ value (480 and 640) since there is the greatest reduction in the w/c ratio (Table 5), the highest increase in the cement hydration degree (Table 3) with a negligible or no increase at all in the air volume. For the polymers having lower $\bar{M}n$ value (260 and 240), both the reduction in the w/c ratio (Table 5) and the increase in the cement hydration degree (Table 3) are much lower, so that the increase in the air volume with respect to the control mortar substantially reduces the above beneficial effects and no significant increase in strength is obtained in superplasticizerd mortars.

Table 5 Characteristics of mortars with a given flow prepared with and without Naphthalene sulfonate polymers of different Molecular Weight ($\bar{M}n$).

$\bar{M}n$ OF POLYMER	WATER/CEMENT RATIO	FLOW (*)	ENTRAINED AIR (%)	COMPRESSIVE STRENGTH 1day	7days	28days
CONTROL	0.46	70	5.0	12.0	42.0	53.5
260	0.43	70	8.0	11.0	49.0	51.0
290	0.43	70	8.2	11.0	43.5	53.0
480	0.40	70	4.5	10.0	52.0	61.0
640	0.39	70	5.0	10.5	53.5	64.0

(*) ASTM C 109 - 5 drops only

Conclusions

By increasing the Molecular Weight of sulfonated Naphthalene polymer the fluidifying effect of the superplasticizer increases. This effect is accompanied with an increase in the zeta potential of cement pastes and in the amount of polymer adsorbed on hydrated cement. For the cement used in the present work no significant increase in fluididity, zeta potential and adsorption appears for Number Molecular Weight ($\bar{M}n$) of the polymer higher than about 600.

By increasing the molecular weight of the polymer, the degree of cement hydration is reduced at earlier ages and increased at later ages. The retarding effect on the early cement hydration, which could be ascribed to the adsorption of polymer molecules on cement particles, seems to be advantageous to reduce slump loss in concrete mixes. The increase of the hydration degree at later ages could be ascribed to a better dispersion of cement particles, as a result of a higher zeta potential which increases by increasing the molecular weight of the polymer.

The molecular weight of the polymer significantly affects also the increase in the volume of entrained air in cement mixes. This volume decreases by increasing the molecular weight of the polymer. With $\bar{M}n$ value higher than about 600 no substantial increase in the air volume is found with respect to the control mix. Consequently the increase in strength caused by polymers with $\bar{M}n$ higher than a certain value (about 600 for the cement used in the present work) becomes very effective as the reduction in the w/c ratio and the increase in the degree of cement hydration are not counteracted by any increase in the volume of entrained air.

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