Superplasticizers and Other Chemical Admixtures in Concrete

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Blending of Acrylic Superplasticizer with Napthalene, Melamine or Lignosulfoate-Based Polymers

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Symopsis: Acrylic polymer (AP) performs better than other superplasticizers based on sulfonated-naphthalene-formaldehyde (SNF), sulfonated-melamine formaldehyde (SMF) or modified lignosulfonate (MLS). It is better than the other superplasticizers in terms of higher initial slump, at equal water-cement ratio (*w/c*), and lower rate of slump loss.

AP, however, is a little more expensive than SMF and much more expensive than either NSF or MLS. Therefore, blending of AP with the other polymers could reduce the cost. The purpose of the present work was to study the influence of binary blended admixture (AP on one hand, and SNF, MSF or MLS on the other one) on the performance of superplasticized concretes in terms of slump, slump loss, specific gravity, air content and compressive strength at equal *w/c*.

The data presented in this paper indicates that there is no practical advantage in blending AP with NSF or MSF. Moreover the combination of AP with NSF seems to be unreliable because produces an erratic reduction in the workability of the concrete mixture when about 75% of AP is replaced by NSF. On the other hand, a combination of AP with MLS appears to perform as well as the pure acrylic polymer in terms of workability, slump loss, air content and strength development, provided that the replacement of AP by MLS is not higher than 25%. Therefore, these blended AP-MLS superplasticizers appear to be very interesting because they are cheaper than the pure acrylic polymer at approximately equal performance.

Keywords: Acrylic resins; compressive strength; lignosulfonate; melamine resins; naphthalene; slump tests; superplasticizers

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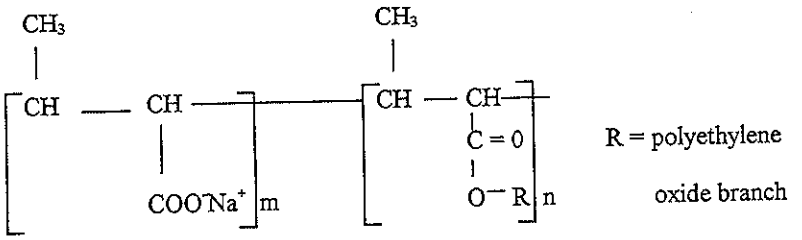
INTRODUCTION

Superplasticizers can be classified into four groups: sulfonated melamine-formaldehyde condensate (SMF); sulfonated naphthalene-formaldehyde condensate (SNF); modified sugar-free lignosulfonate (MLS) and others including polyacrylates, sulfonated polystyrene, etc.

Combination of different superplasticizers have been investigated (1). For instance, blending of MLS with SMF or SNF has economical advantages since MLS is cheaper than SMF and SNF. A blend of SNF and SMF may be used to increase early strength with respect to SNF alone (2).

More recently (3-5) an acrylic polymer (AP) has been developed with better performances in terms of higher reduction of mixing water and lower rate of slump loss. The chemical structure of this AP is given below.



The cost of AP is higher than that of SNF, SMF and MLS. Since commercial products of these polymers are available in different concentrations of aqueous solutions (40% for NSF; 30-40% for SMF; 30-50% for MLS and 30% for AP) the comparative costs of these four materials are refered to 1 kg of dry polymer (Table 1). These data are based on the cost of the raw materials presently available in Italy, and can change a little in other countries.

The purpose of present paper is to study the performance of a combined chemical admixture based on AP and one of the other available superplasticizers: SNF, SMF and MLS.

MATERIALS

Although many brands and types of cement were tested, for the sake of brevity only the results of two typical cements will be discussed: a pure portland cement for precast concrete and a portland-limestone blended cement for ready mixed concrete (CE I 42.5 R and CE II/A-L 42.5 R respectively according to the ENV 197/1 European standard norm). Table 2 shows the properties of these two cements. The results of the superplasticized mixtures with these two cements are representative of the concrete behaviour of many other cements.

Sand with a fineness modulus of 2.6 and gravel (5-32 mm) were used with a proportion of 45.7% of sand and 54.3% by mass respectively.

Superplasticizers in form of the following polymer aqueous solutions were used:

N = 40% SNF + 60% water

M = 40% SMF + 60% water

L = 40% MLS + 60% water

A = 30% AP + 70% water

Binary combinations of A with N, M or L were studied. For instance, in the A-N combination 0-25-50-75-100% of A with 100-75-50-25-0% of N respectively were tested.

Table 3 shows the composition and the properties of the two reference concrete mixtures without the addition of superplasticizers. Both mixtures were no-slump concretes with a water-cement ratio of about 0.50. By using a dosage of 1% by cement mass of pure or blended superplasticizers the slump level of the concrete mixtures was in the range o 50-250 mm just after mixing.

METHODS

After initial mixing for 5 min in a laboratory drum mixer, specific gravity, slump and air content were measured in accordance with ASTM C138, C143 and C231, respectively. These measurements were carried out on concrete placed in three layers of approximately equal volume and then rodded with 25 strokes for each layer.

The slump-loss behaviour of each superplasticized concrete mixture was studied by measuring the slump level at various times up to 60 min after initial mixing. Prior to re-measurement of slump, concretes were mixed for a period of 2 minutes.

Cube specimens were manufactured from the concrete mixtures mixed for the initial 5 min. They were rodded and cured at 20°C with R.H. of 95%. The compressive strength was measured at 1, 7 and 28 days.

RESULTS

Table 4 shows specific gravity and air content of all the concrete batches manufactured with pure portland cement (CE I 42.5 R) or blended portland-limestone cement (CE II/A-L 42.5 R). The initial air content of concrete mixtures with pure lignosulfonate or with blended 50% L superplasticizers was significantly higher than all the other superplasticized concretes. However after 15 min, most of this unstable air was lost.

The results in terms of slump increase and slump-loss for fresh mixtures and in terms of compressive strength for hardened concrete will be examined for each of the following combination: *A-N*, *A-M* and *A-L*.

ACRYLIC-NAPHTHALENE COMBINATION

In some cases concrete producers use a combination of acrylic and naphthalene superplasticizers in order to reduce the cost of the chemical admixture for a superplasticized concrete with a low rate of slump-loss. However, under some circumstances, the effect produced was worse than that expected for the individual superplasticizers. One of the purpose of the present work was to confirm this effect and to identify the circumstances under which it occurs, if any. Figures 1 and 2 show the slump-loss curves of superplasticized concretes with pure portland cement (CE I 52.5 R) and blended portland-limestone cement (CE II/A-L 42.5 R) respectively. The pure acrylic polymer (*A*) performed better than the pure naphthalene (*N*) superplasticizer in terms of

higher initial slump level and lower slump-loss. In general, when *A* was replaced by *N* in the blended superplasticizers the initial slump level of the concrete mix was reduced and the slump-loss was increased, in comparison to the performance of each individual polymers. However, a sort of antithetical effect (as the opposite of synergic) was surprisingly recorded for the slump of the concrete mix with the CE II/A-L 42.5 R cement (Fig. 2): when the superplasticizer composition was 25% of *A* and 75% of *N*, this specific blended superplasticizer performed significantly worse than any other blended superplasticizers or pure individual polymers. This effect, is more evident when the slump at different mixing times is plotted as a function of the *A-N* superplasticizer composition (Fig. 3).

According to the data shown in the present paper, one could conclude that the antithetical composition effect of the superplasticizer (25% *A* - 75% *N*) is found for concrete mixtures containing blended portland-limestone cement (Fig. 3) and not pure portland cement (Fig. 4). However, this is not necessarily true since, by changing the source of a given cement type, the antithetical composition effect occurred erratically and independently of the type or strength class of the cement. In some cases, even batches of the same cement type and coming from the same source, but stored for different periods of time, performed erratically with or without the antithetical composition effect of the *A-N* blended superplasticizer.

Although this effect was erratic, when it occurred it happened always at the same acrylic-naphthalene composition, i.e. 25% *A* and 75% *N*. Moreover, blended liquid superplasticizers (A = 50-75%) appeared to be more viscous than the aqueous solutions of the individual polymers (6). However, the higher viscosity of blended *A-N* superplasticizers seems to be the effect of a chemical change rather than the direct cause of a lower slump level of the corresponding concrete mixture. It is reasonable to assume that there is some chemical change reaction between AP and SNF which reduces the superplasticizing effect in the presence of concurrent factors related with the composition of cement and its period of storage before its use.

Although the available data of this paper cannot explain the mechanism of the antithetical *A-N* composition effect and why it is so erratic, from a pratical point of view these data are able to explain why, under some circumstances, the combined use of AP and SNF on concrete batching plants performed worse than that of each individual superplasticizer.

Figure 5 indicates the compressive strength results of the concrete mixtures shown in Table 3 in the absence and in the presence of the pure *A* or *N* superplasticizer. The compressive strength of concretes with *A-N* blended superplasticizers are between those of the pure *A* and *N* polymers.

At equal *w/c*, superplasticized concretes attained to approximately the same strength level. Compressive strength of reference mixtures, particularly at later ages, were lower than those of the corresponding superplasticized concrete. This seems to be related with a better dispersion of cement particles in superplasticized mixtures and therefore with a higher degree of hydration particularly at later ages.

ACRYLIC-MELAMINE COMBINATION

Figures 6 and 7 show the slump-loss curves of superplasticized concretes with pure portland cement and blended portland-limestone cement, respectively. The pure acrylic polymer (*A*) performed better than the pure melamine (*M*) superplasticizer in terms of higher initial slump level and lower rate of slump loss. The performance of blended *A-M* superplasticizers decreased when the content of *M* was increased. This was true for all the cements examined. In other words, the antithetical composition effect, which sometimes was recorded for the *A-N* blended superplasticizer (Fig. 2 and 3), was not found for the *A-M* blended polymers regardless of the cement used in the present work.

The effect of *A* and *M* superplasticizers on the compressive strength development of the concrete mixtures at equal *w/c* was the same as that found with *A* and *N* chemical admixtures, except for the higher 1 day strength when pure melamine polymer was used specially in combination with blended portland-limestone cement (Fig. 8).

ACRYLIC-LIGNOSULFONATE COMBINATION

Figures 9 and 10 show slump loss curves for pure and blended *A-L* superplasticizers. Again, pure acrylic polymer performed better than pure lignosulfonate in terms of higher initial slump. However, the difference was smaller than that recorded in the *A-N* or *A-M* combination. It seems that the initial slump level of pure *L* treated concretes was relatively high due to the very high air content in form of large bubbles (Table 4). The subsequent slump loss of this concrete was substantially due to the loss of part of this unstable air (Table 4).

The blended superplasticizer with 25% of *L* performed quite well in terms of high initial slump level and negligible slump loss up to 60 min. Moreover, since the air content of the concretes with this *A-L* blended superplasticizer was as low as that of the other acrylic superplasticized concrete mixtures (< 2%), even the strength development was as good as that of the pure acrylic concretes (Fig. 11). This result appears to be very interesting in view of the lower cost of lignosulfonate with respect to that of the acrylic polymer (Table 1).

With higher lignosulfonate contents, the slump loss was more remarkable (Fig. 9-10) and the strength was reduced to a level lower than that of the reference mix (Fig. 11).

CONCLUSIONS

Pure acrylic polymer performed better than individual superplasticizers (based on naphthalene, melamine and modified lignosulfonate) in terms of higher initial slump level and lower slump loss. Compressive strength at equal *w/c* of all superplasticized concretes was approximately the same, except that of concretes with high lignosulfonate content which was lower because of the presence of air in form of macro-bubbles.

There is no advantage in blending acrylic polymer with naphthalene superplasticizer since workability is reduced and slump loss is increased by decreasing the acrylic component. Moreover, under specific circumstances (25% *A* - 75% *N*), there is a surprisingly reduced performance for this blended superplasticizer in terms of lower slump with respect to the individual pure components. This reduction in performance was erratic and could not be explained on the basis of the available data. Due to this unreliable behavior, blending of acrylic and naphthalene superplasticizers should not be encouraged.

No specific advantage appeared in using combined acrylic-melamine superplasticizers, since the performance of these blended admixtures was intermediate between those of the individual components and the cost of *M* (40% aqueous solution) is even higher than that of *A* (30% aqueous solution).

Blended acrylic-lignosulfonate superplasticizers appeared to perform approximately as well as pure acrylic, provided that the amount of the acrylic component was at least 75%. No change in slump loss, air content and strength was recorded for a 75% *A* - 25% *L* blended superplasticizer with respect to the pure acrylic component. Since lignosulfonate is much cheaper than the acrylic polymer, this blended superplasticizer appears to be useful from an economic point of view.

ACKNOWLEDGEMENT

The work in preparing the text and the Figures by Romina Boaretto and Alessandra Galletti is acknowledged.

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TABLE 1 —COMPARATIVE COSTS OF SUPERPLASTICIZERS IN PERCENTAGE WITH RESPECT TO THAT OF 1kg OF DRY ACRYLIC POLYMER

Type of Superplasticizers	**Concentration of the aqueous solution**	**Cost of aqueous solution**	**Cost of dry polymer**
A	30% AP	30	100
M	40% SMF	32	80
N	40% SNF	16	40
L	40% MLS	8	20

TABLE 2 —MINERALOGICAL COMPOSITION AND PROPERTIES OF CEMENTS

Composition (%)	**Cement CE I 42.5 R**	**Cement CE II A/L 42.5 R**
C_3S	46	43
C_2S	30	20
C_3A	8	5
C_4AF	7	5
$CaSO_4 \cdot 2H_2O$	5	4
$CaCO_3$	2	20
Blaine finessess (m^2/kg)	390	450
Compressive strength (MPa):		
at 2 days	28.2	20.3
at 28 days	48.7	47.4

TABLE 3 —COMPOSITION AND PROPERTIES OF THE REFERENCE CONCRETE MIXTURES

Composition/Property	Mixture with cement:	
	CE I 42.5 R	CE II/A - 42.5 R
Cement (kg/m^3)	348	350
Water (kg/m^3)	174	168
Sand (kg/m^3)	864	867
Gravel (kg/m^3)	1028	1031
w/c	0.50	0.48
Slump (mm)	15	10
Air (% by vol.)	1.4	1.6
Compressive Strength (MPa) at:		
1 day	25.2	14.5
7 days	42.5	40.0
28 days	51.0	49.8

TABLE 4 —AIR CONTENT AND SPECIFIC GRAVITY OG CONCRETE MIXTURES AFTER MIXING (5 MIN.)

CONCRETE MIXTURE	With CE I 42.5 R Cement		With CE II/A-L 42.5 R Cement	
	Specific gravity (kg/m^3)	Air volume (%)	Specific gravity (kg/m^3)	Air volume (%)
Reference	2414	1.4	2416	1.6
A (100%) - *N* (0%)	2435	1.7	2410	1.9
A (75%) - *N* (25%)	2440	1.6	2425	1.8
A (50%) - *N* (50%)	2445	2.4	2425	2.0
A (25%) - *N* (75%)	2435	2.2	2438	1.6
A (0%) - *N* (100%)	2440	2.0	2442	1.5
A (100%) - *M* (0%)	2443	1.8	2444	1.1
A (75%) - *M* (25%)	2438	1.8	2440	1.7
A (50%) - *M* (50%)	2446	1.7	2448	1.5
A (25%) - *M* (75%)	2448	1.7	2425	1.9
A (0%) - *M* (100%)	2442	1.7	2437	1.8
A (100%) - *L* (0%)	2425	1.8	2423	1.4
A (75%) - *L* (25%)	2420	2.0	2413	1.8
A (50%) - *L* (50%)	2410	2.9	2387	2.9
A (25%) - *L* (75%)	2360	4.4*	2343	4.9*
A (0%) - *L* (100%)	2212	> 8*	2221	> 8*

* *less than 2.5% after 15 min of mixing.*

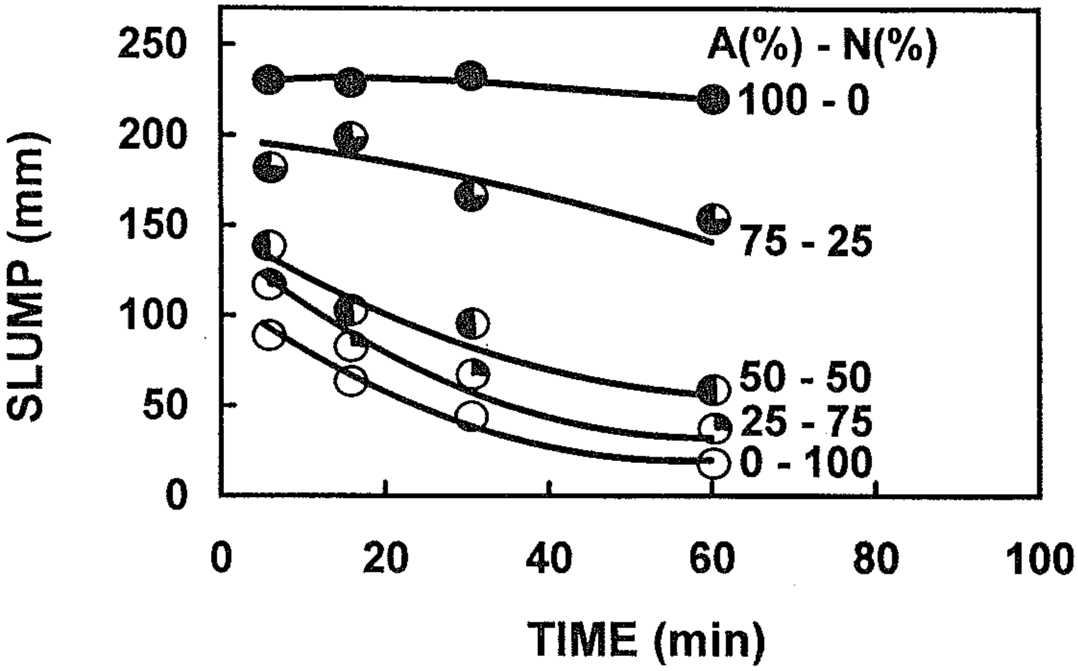

Fig. 1—Slump loss of concretes with CE 42.5R cement as a function of the acrylic (A)-Naphthalene (N) superplasticizer composition

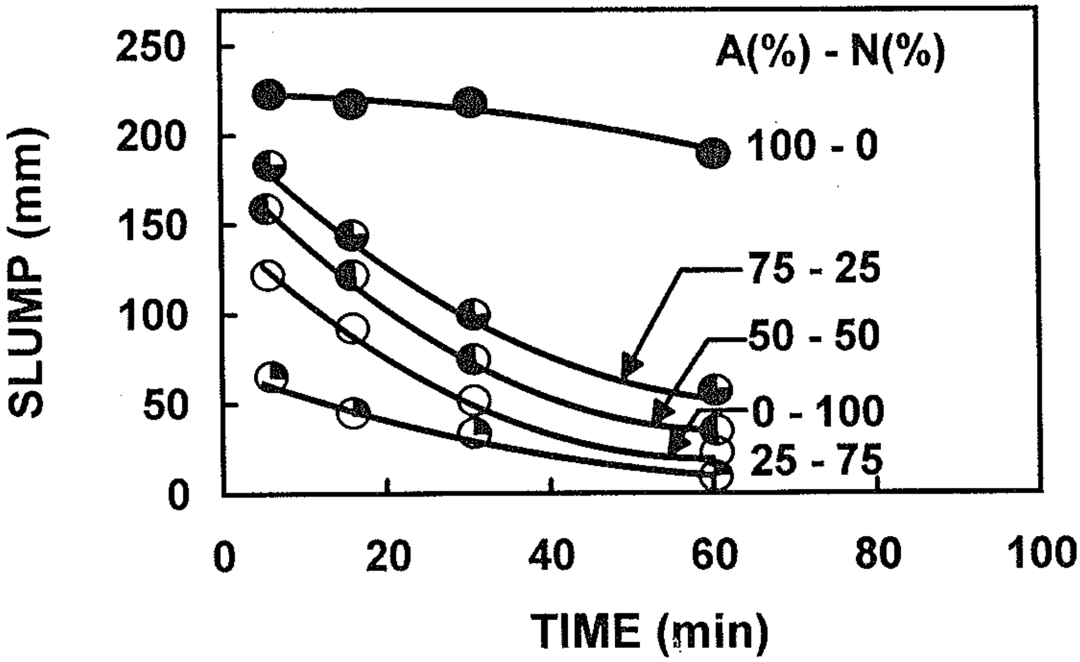

Fig. 2—Slump loss of concretes with CE II/A-L 42.5R cement as a function of the acrylic (A)-Napthalene (N) superplasticizer composition

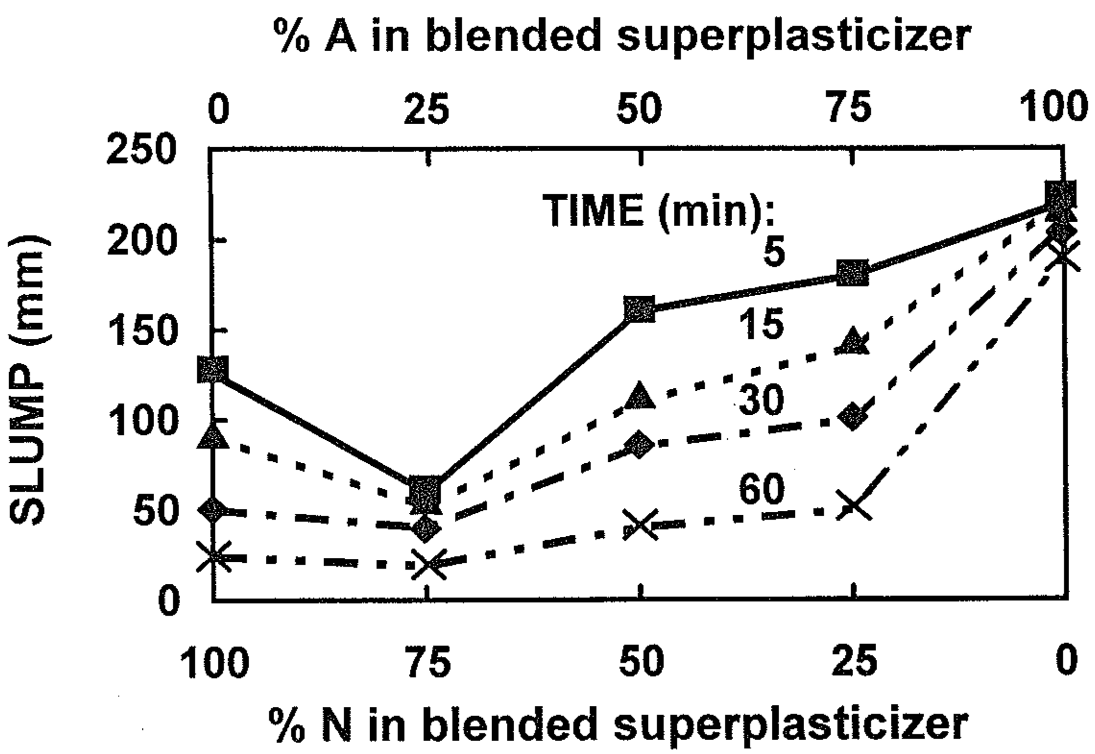

Fig. 3—Influence e of the acrylic (A)- naphthalene (N) superplasticizer composition on the slump of concretes with blended portland-limestone cement (CE II/A-L 42.5R)

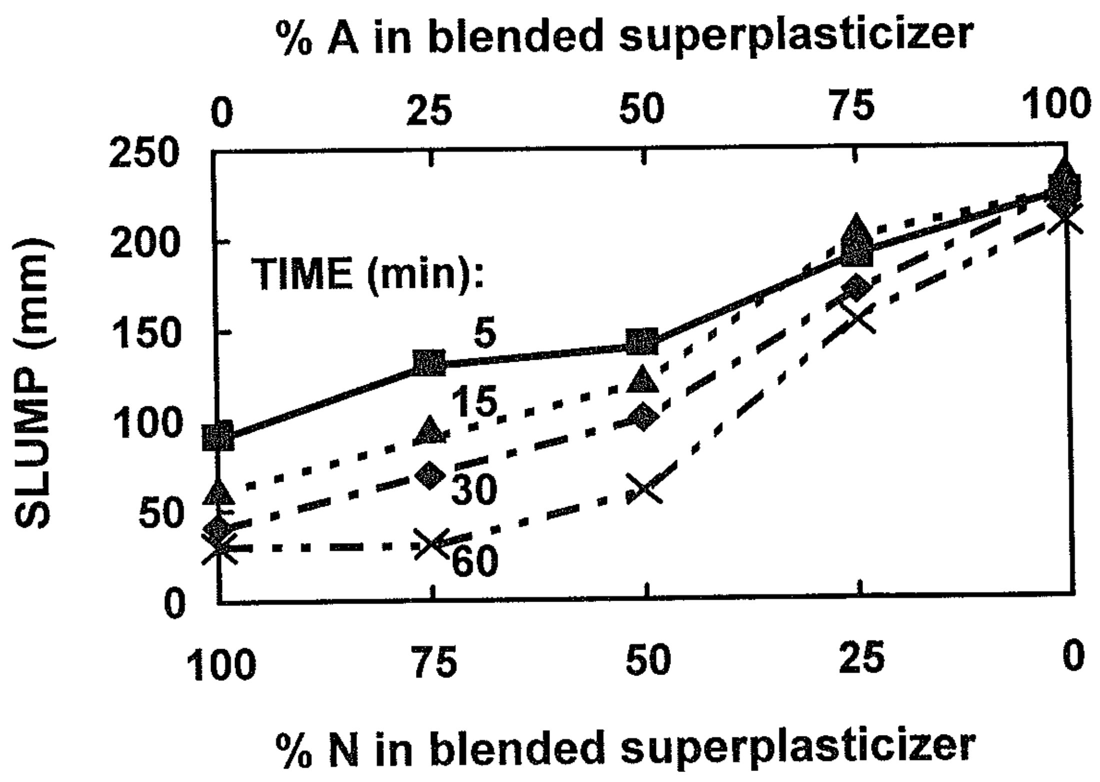

Fig. 4—Influence of the acrylic (A)- naphthalene (N) superplasticizer composition on the slump of concretes with pure portland cement

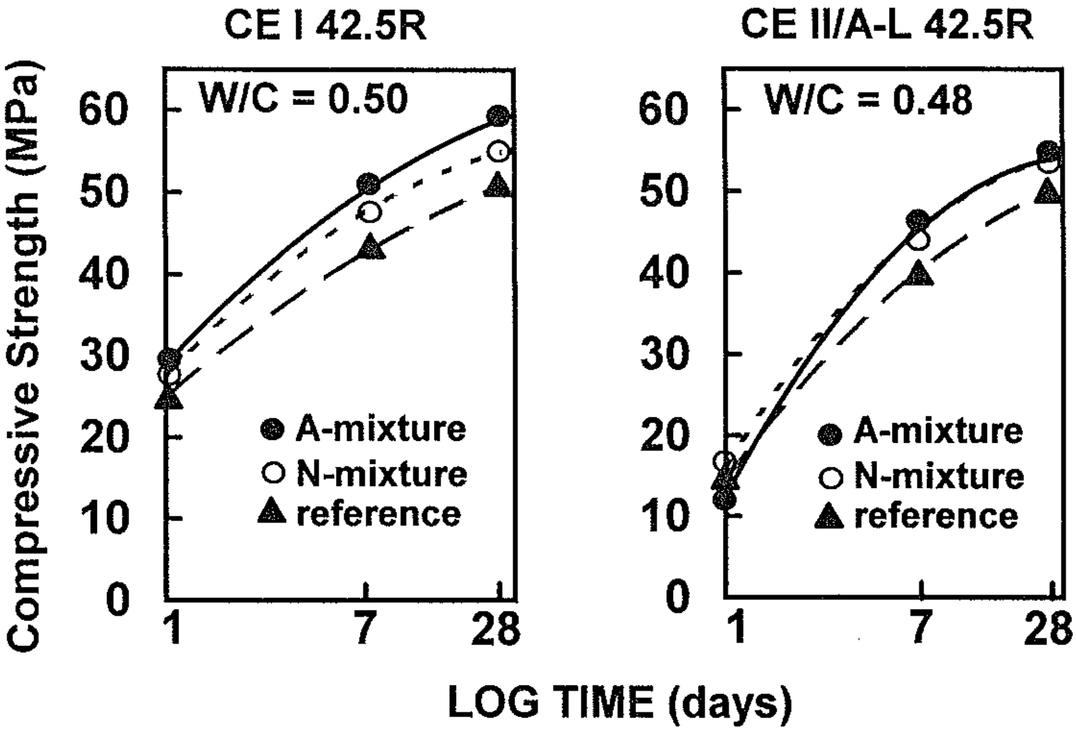

Fig. 5—Compressive strength versus time for concretes with pure polymers A and N: strength values of concretes with blended superplasticzers are between those with pure polymers

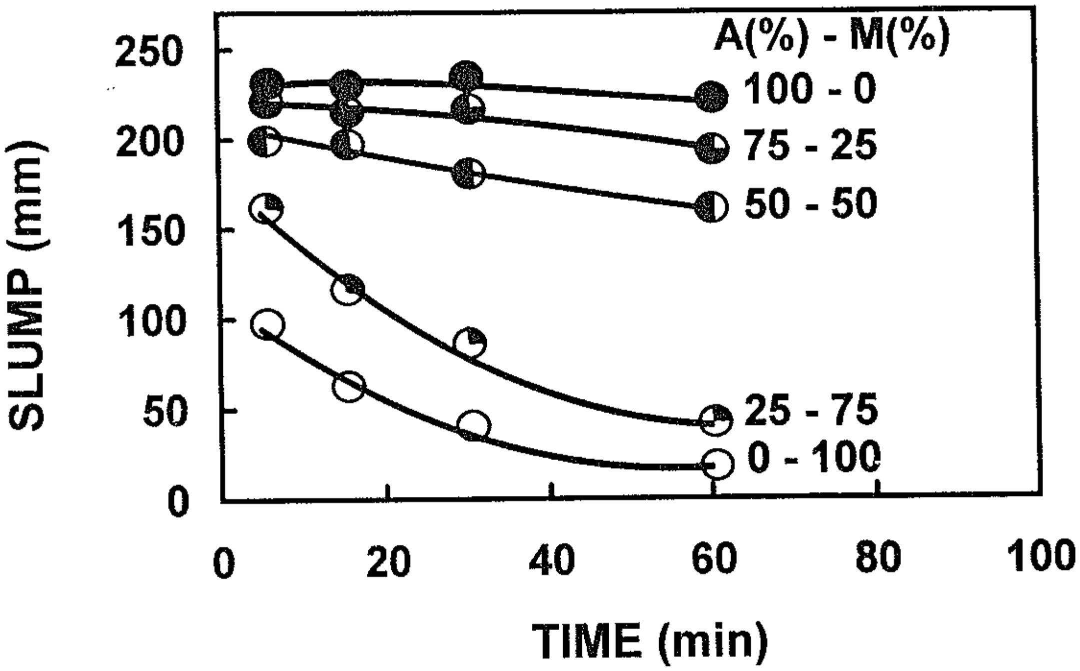

Fig. 6—Slump loss of concretes with CE I 42.5R cement as a function of the acrylic (A)-melamine (M) superplasticizer composition

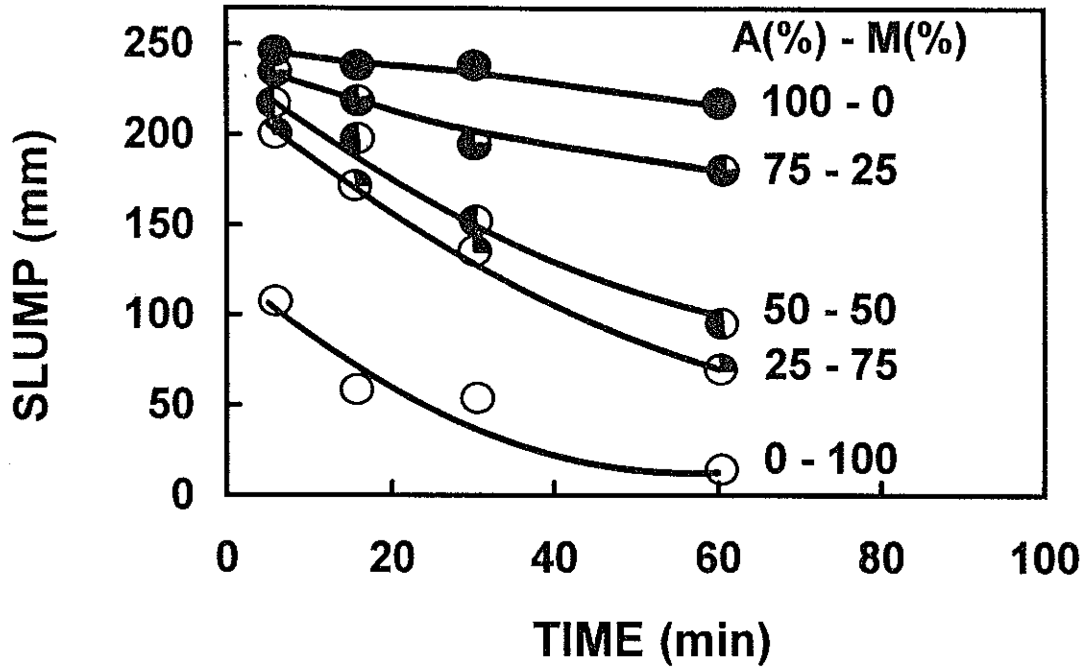

Fig. 7—Slump loss of concretes with CE II/A-L 42.5R cement as a function of the acrylic (A)- melamine (M) superplasticizer composition

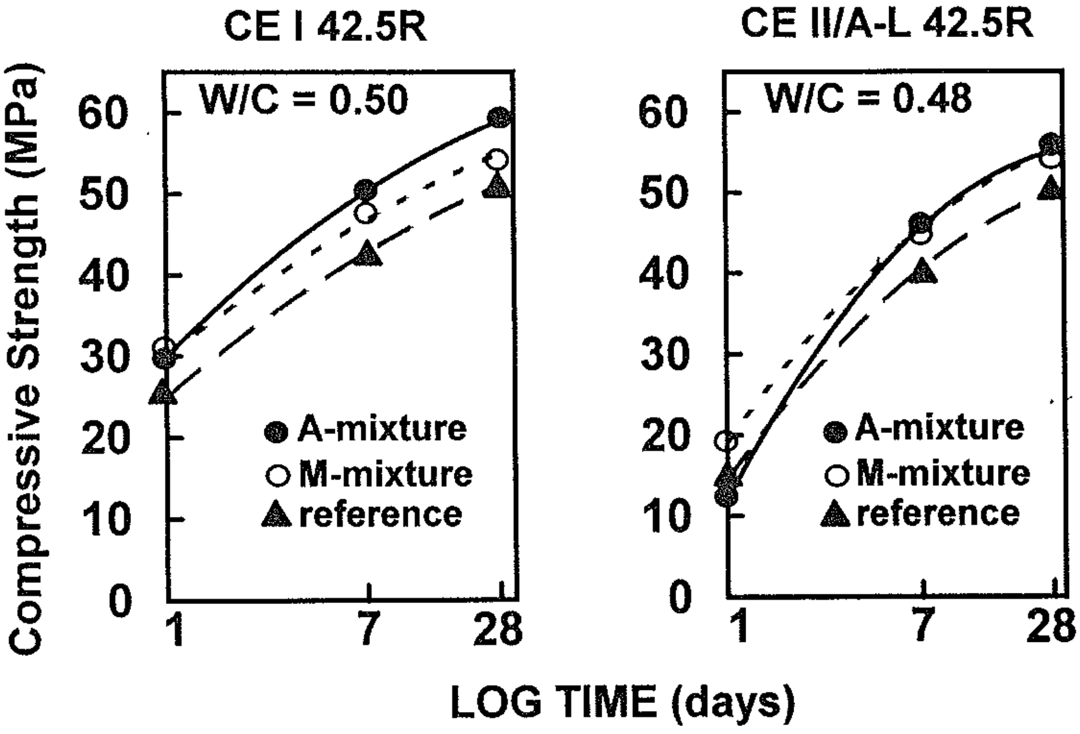

Fig. 8—Compressive strength versus time for concretes with pure polymers A and M: strength values of concretes with blended superplasticizers are between those with pure polymers

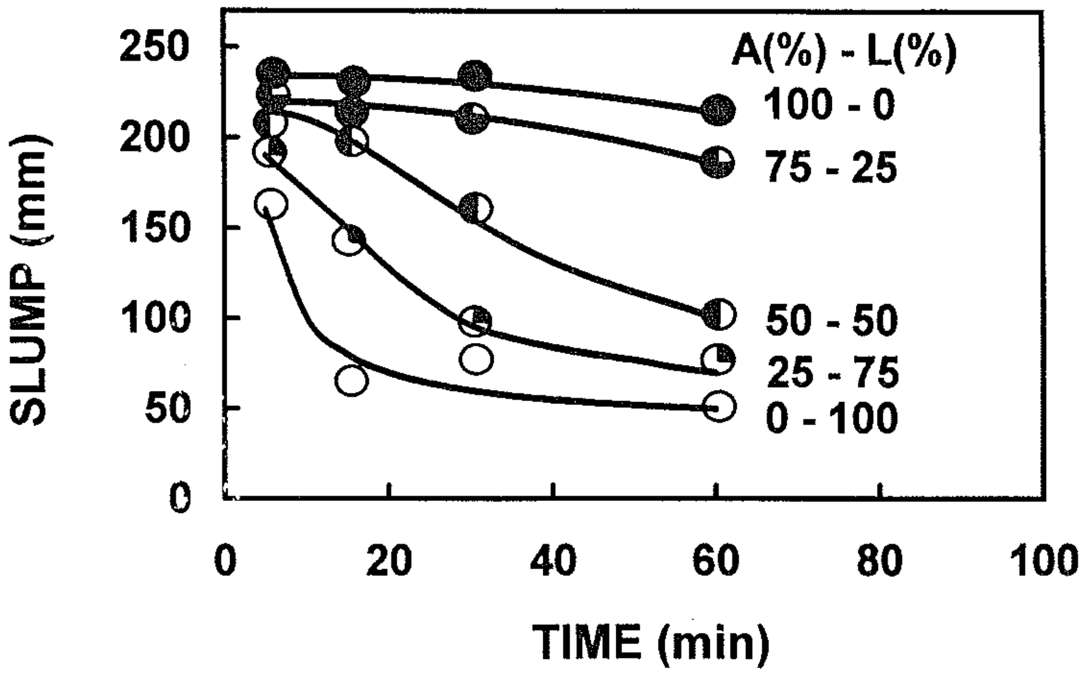

Fig. 9—Slump loss of concretes with CE I 42.5R cement as a function of the acrylic (A)- lignosulfate (L) superplasticizer composition

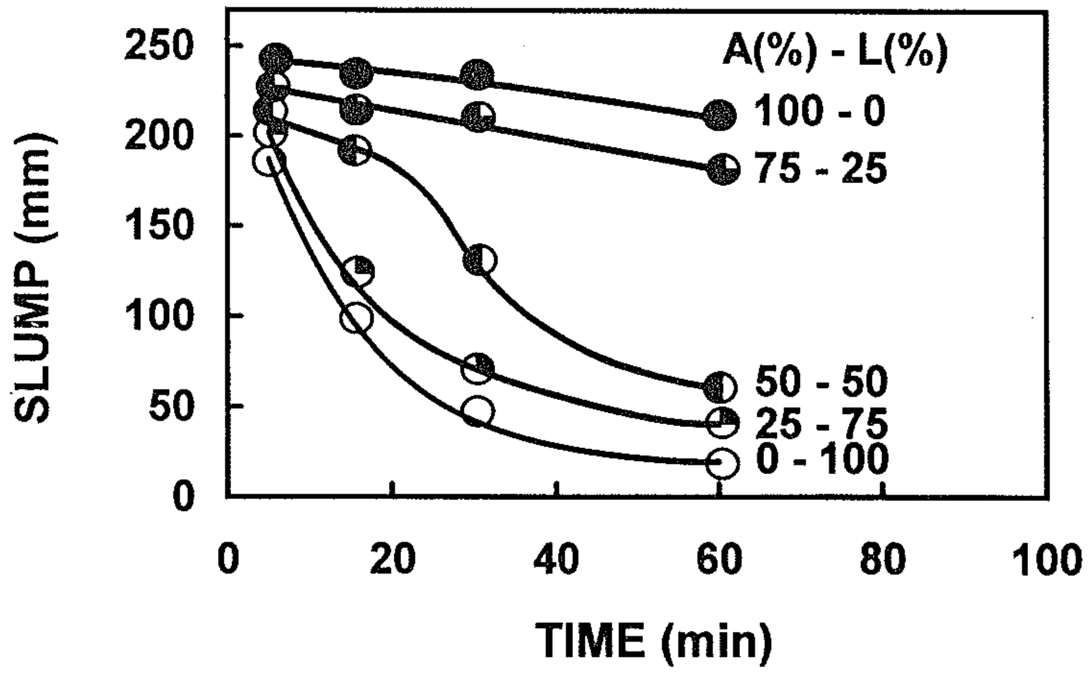

Fig. 10—Slump loss of concretes with CE II/A-L 42.5R cement as a function of the acrylic (A)- lignosulfate (L) superplasticizer composition

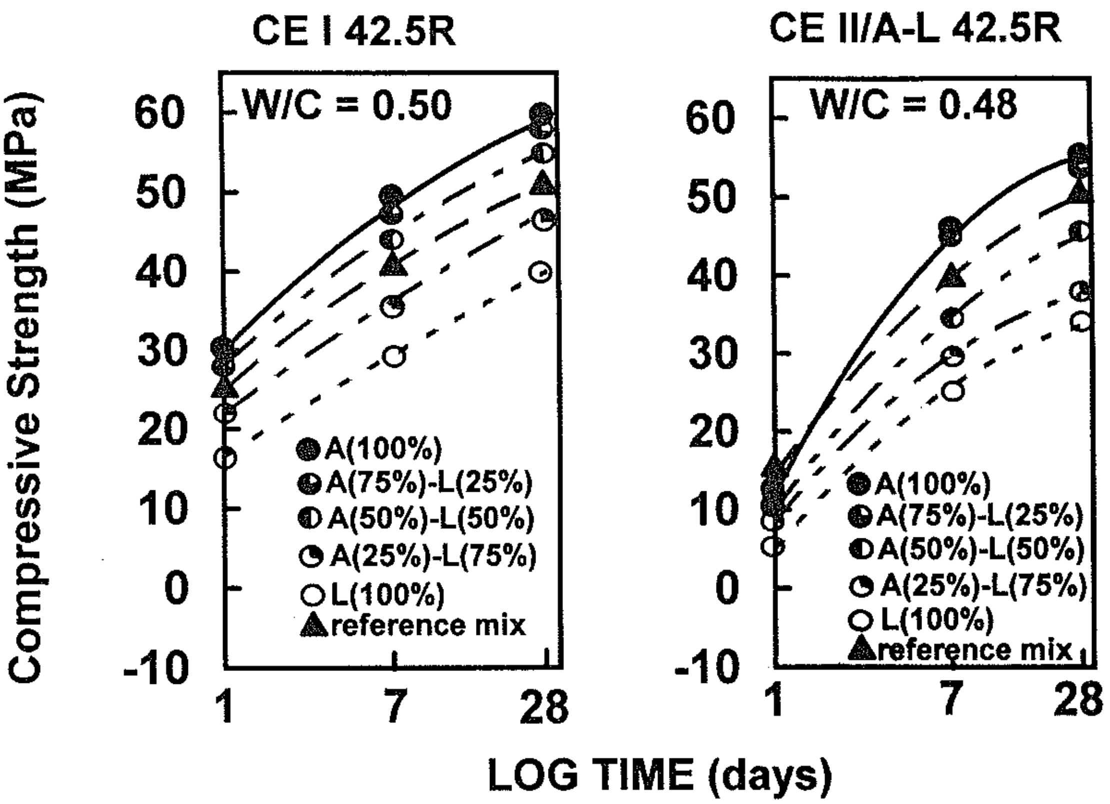

Fig. 11—Compressive strength versus time for concretes with blended A-L superplasticizers