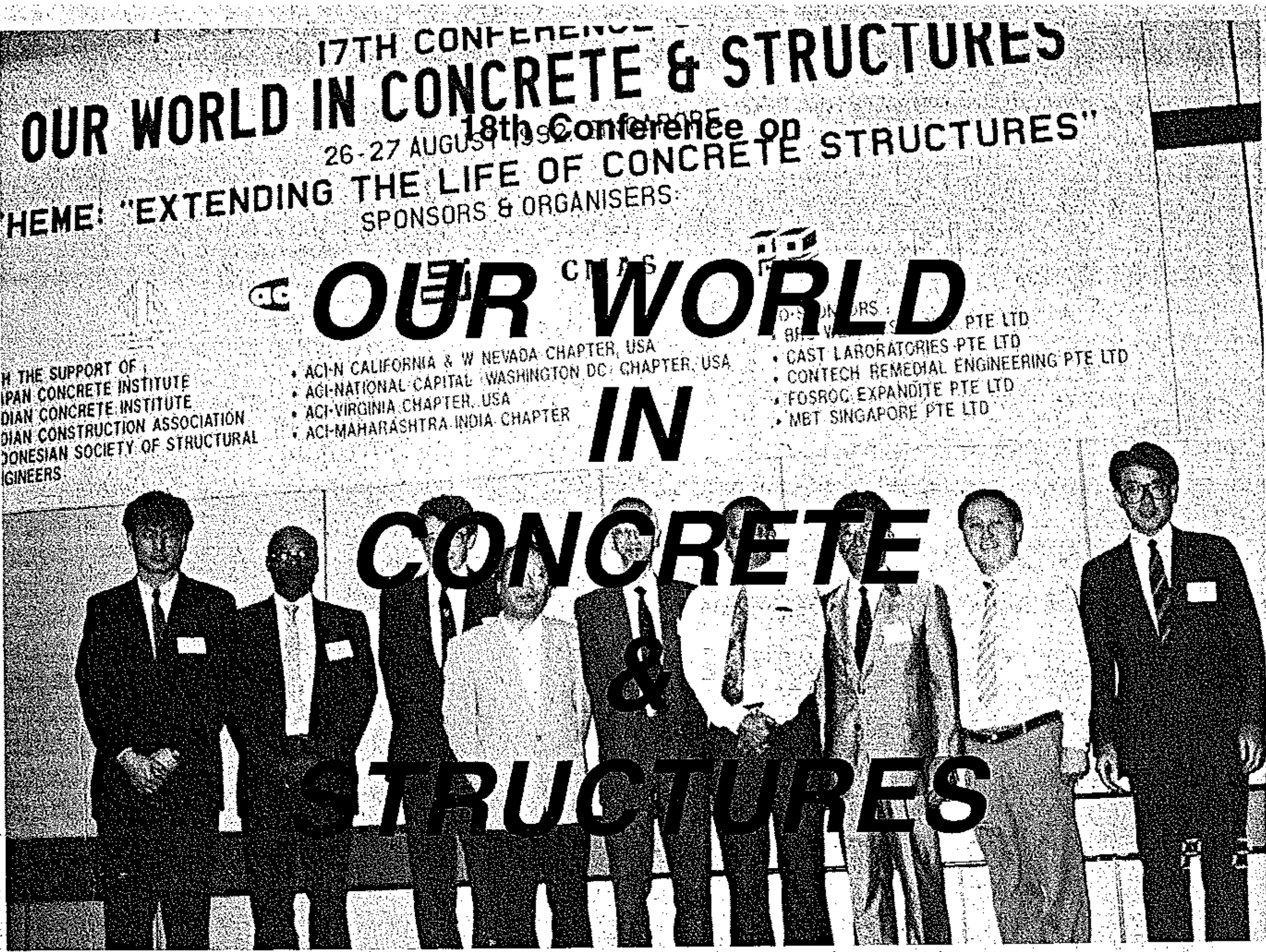
18th Conference on

OUR WORLD IN CONCRETE & STRUCTURES



25 – 27 August 1993
Singapore

Theme: "QUALITY IN CONCRETE & STRUCTURES"

Conference Documentation
Volume XII

Sponsors & Organisers:

READY-MIXED CONCRETE ASSOCIATION OF SINGAPORE — AMERICAN CONCRETE INSTITUTE SINGAPORE CHAPTER — SINGAPORE CONCRETE INSTITUTE — CEMENT MANUFACTURERS' ASSN OF SINGAPORE — PRESTRESSED & PRECAST CONCRETE SOCIETY — PREMIER CONFERENCE

With the support of:
* Japan Concrete Institute
* Indian Concrete Institute
* Indian Construction Association
* Indonesian Society of Structural Engineers
* International Association of Concrete Repairs Specialist, USA
* ACI-N California & W Nevada Chapter, USA
* ACI-National Capital (Washington DC) Chapter, USA
* ACI-Virginia Chapter, USA
* ACI-Maharashtra India Chapter
* CSIRO-Div. of Building, Construction & Engineering, Australia

18th Conference on OUR WORLD IN CONCRETE & STRUCTURES
25-27 August, 1993: Singapore

Zero slump-loss superplasticized concrete

M. Collepardi, L. Coppola, Enco, Italy
T. Cerulli , G. Ferrari , C. Pistolesi , P. Zaffaroni, Mapei, Italy
F. Quek, Mapei Far-East, Singapore

ABSTRACT

A research program, including physico-chemical and technological laboratory tests as well as field tests, has been carried out to study a new type of concrete superplasticizer based on the carboxylic acrylic ester (CAE) copolymer in comparison with sulfonated melamine or naphtalene formaldehyde condensate type (SMF or SNF).

The CAE copolymer can be used to manufacture zero slump-loss superplasticized concrete for a transportation time of at least 2 hours even at lower dosage than that usually utilized for MSF or NSF based admixtures.

The compressive strength of CAE treated concrete is higher than that of the corresponding mixes with MSF of NSF polymers at early ages and to a greater extent at later ages, independently of the curing temperature.

The mechanism of the CAE copolymer has been studied to explain the more effective superplasticizing action and the lower slump-loss effect by examining the adsorption zeta potential and X-ray diffraction analysis results.

1.0 INTRODUCTION

All the properties of hardened concrete, including strength and durability can be improved by reducing the water/cement (w/c) ratio. However, at a given cement content (c), the reduction in mixing water (w) decreases the fresh mix workability so that concrete placing becomes very difficult at the work site. Therefore, special chemical admixtures (superplasticizers) are used to place low w/c ratio concretes without sacrificing the workability of fresh mixes, particularly those devoted to high quality concrete structures.
The main components of the superplasticizers are substantially based on sulfonated melamine formaldehyde (SMF) condensate type or sulfonated naphtalene formaldehyde (SNF) condensate type in form of a 40% aqueous solution [3]. Both of these admixtures, at a dosage of about 1% by weight of cement, are able to transform a no-slump concrete into a self-levelling mix with a slump increase of about 200 mm. However, when concrete mix should be transported for a long time, particularly in hot weather, the initial slump level is lost to a significant extent.
Since slump-loss is un-avoidable because of the intrinsic requirement for cement mixes which should set and harden in a relatively short time, a right and proper compromise would be a zero slump-loss concrete mix for 1-2 hours.
Fujiu et al. [5], Fukuda et al. [6], Yamakawa et al. [9] and Mitsui et al. [7] have studied alternative chemical composition to limit the slump-loss problem. Many of these superplasticizers are mainly based either on bicomponent admixtures containing the SNF polymer and a reactive polymer (in form of an insoluble precursor) as a slump-loss reducer [6, 7, 9], or a monocomponent polymer which is not soluble in mixing water but, under the alkaline environment formed in the aqueous phase in contact with cement, is slowly trasformed into an aqueous soluble product having superplasticizing effect [5].
The purpose of the present work was to develop and examine a new water soluble monocomponent superplasticizer, based on carboxylated acrylic ester (CAE) copolymer, which is able to give a superplasticized concrete mix with low w/c ratio without significant slump-loss for 1-2 hours of the fresh mix and strength reduction at early as well as at longer ages of the hardened concrete.

2.0 EXPERIMENTAL

In the present paper the experimental results concerning the three following section will be shown:

(i) physico-chemical tests on the mechanism of the new superplasticizer;
(ii) laboratory tests on concrete technology;
(iii) field tests on concrete transportation.

For each of the above three sections the CAE copolymer (in form of a 30% aqueous solution) will be examined in comparison with the other two main polymers (SMF and SNF in form of a 40% aqueous solution) usually utilized all over the world to produce superplasticized concretes. Figure 1 shows the chemical composition of the CAE copolymer beside the other two well known chemical polymers (SMF and SNF). The main difference between the new superplasticizing copolymer and the others is that the CAE copolymer contains carboxylic (COO^-) instead of sulfonic (SO_3^-) anionic groups as those present in the SMF or SNF polymers. An other important difference is the molar ratio of negative anionic groups (COO^- or SO_3^-) per organic monomer unit (melamine, or naphtalene or acrylic group) which is 1 for SMF or SNF polymers and much lower than 1 in the CAE copolymer ($m/(m + n) < 1$).

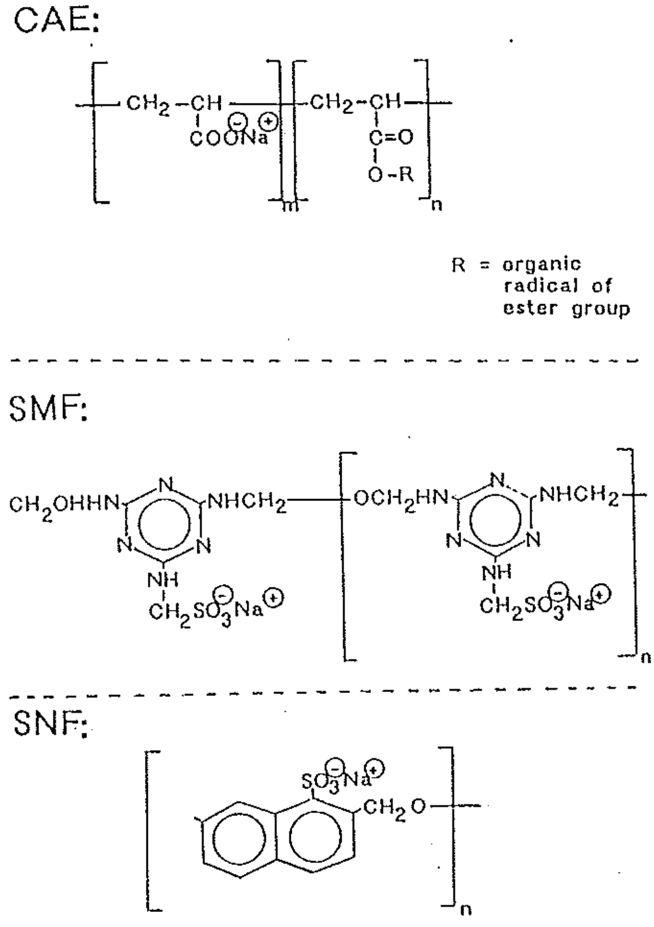


Fig. 1: Chemical composition of CAE copolymer and SMF or SNF polymers.

2.1 PHYSICO-CHEMICAL TESTS ON THE MECHANISM OF SUPERPLASTICIZERS

The fluidizing effect of superplasticizers has been basically related [3] to the three following physico-chemical phenomena: dispersion, adsorption and electrical repulsion (zeta potential).
Superplasticizers cause dispersion into smaller agglomerates of cement particles which predominate in the cement paste of the concrete mix. The dispersion effect is generally ascribed to the polymer adsorption on the cement surface and consequently to the development of the same electrostatic (negative) charge on the cement particles. Therefore, the attractive forces existing among cement particles and causing agglomeration would be neutralized by adsorption of anionic polymers negatively charged, such as SNF or SMF for the SO_3^- group, on the surface of cement particles.
The experimental results of the present work do not confirm this mechanism for the superplasticizing action of the CAE, as it will be demonstrating later.
The fluidity of portland cement mortar mixes with w/c ratio of 0.40 and sand/cement ratio of 3 has been measured (at 5 min) in the absence or in the presence of CAE, SMF or SNF polymers with different dosages of admixtures (0.2-0.6% of dry polymer by weight of cement). Figure 2 shows the flow table measurements of these mortars and indicates that the CAE copolymer performs much more effectively than the SMF or SNF polymers.

The aqueous phase of portland cement pastes (w/c = 2) has been analyzed by the total organic combustion (TOC) technique [1] to determine the residual concentration of polymer after 5 min of agitation, so that the content of admixture adsorbed on cement has been calculated. Figure 3 shows the percentage of polymer adsorbed as a function of the admixture dosage expressed as percentage of dry polymer by weight of cement. The adsorption of CAE copolymer (about 85%) appears to be a little higher than that recorded for the SMF (about 80%) or SNF (75%) polymers.

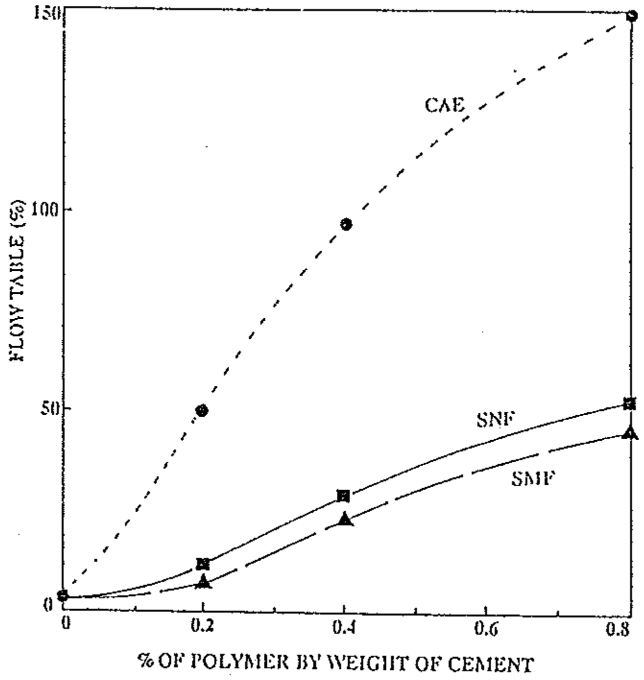


Fig. 2: Influence of CAE, SMF or SNF polymers on the fluidity of portland cement mortar mixes (w/c = 0.40).

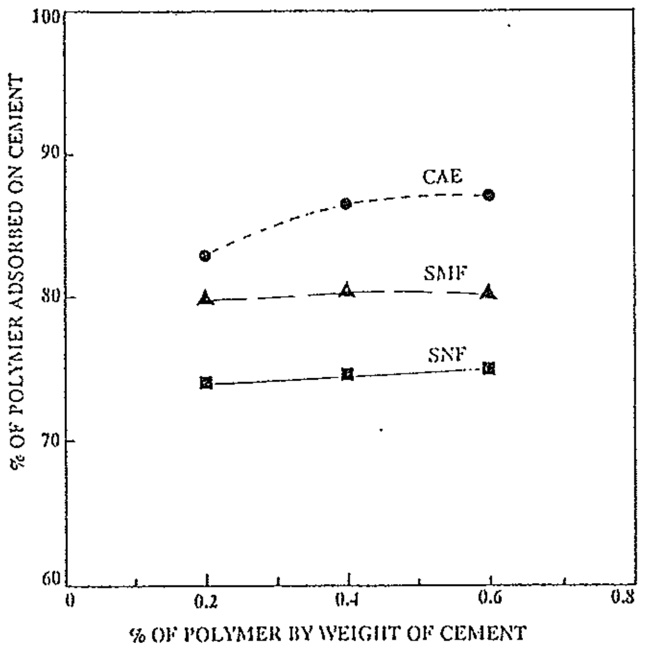


Fig. 3: Adsorption of CAE , SMF and SNF on cement as a function of polymer dosage by weight of cement.

Figure 4 shows the results of zeta potential measurements on the same portland cement pastes determined by the multiangle electrophoretic light scattering (ELS) technique [8]. The zeta potential of cement particles treated by CAE appears to be much lower than those recorded in the presence of SMF or SNF. In particular, when 0.3% of CAE by weight of cement is used, the cement particles appear to be electrically neutral even though the corresponding mortar mix, with the same percentage of admixture (0.3%), is much more fluid than the plain mix and those with SMF or SNF polymers (Fig. 2).

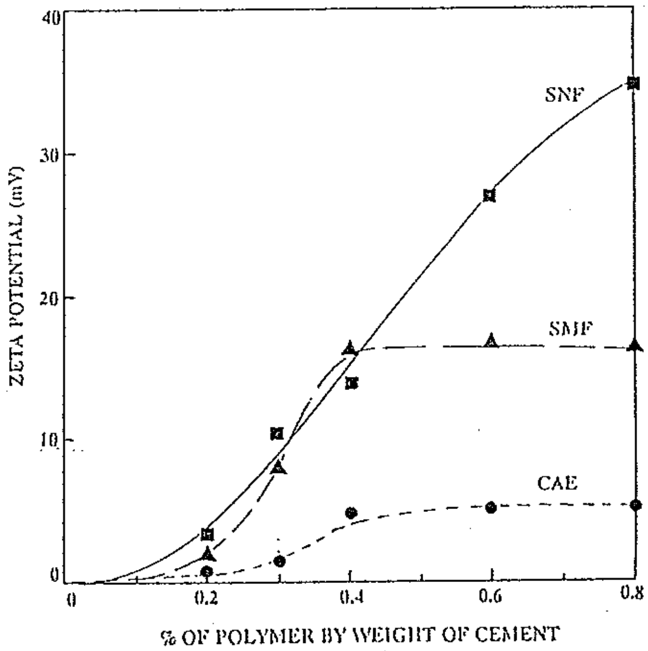


Fig. 4: Zeta potential of CAE, SMF and SNF cement pastes as a function of polymer dosage by weight of cement.

All these results would indicate that the dispersion of cement particles, responsible for the fluidity increase caused by superplasticizer (Fig. 2), is not necessarily related to the electrostatic repulsion associated with zeta potential measurements (Fig. 4). It would seem that, at least for the CAE admixture, the polymer adsorption (Fig. 3) rather than the electrostatic repulsion is responsible for the dispersion of large agglomerates of cement particles into smaller ones and then for the the remarkable increase in the fluidity of cement mixes.
The different mechanism of superplasticizing action performed by the CAE polymer could be related more to a steric hindrance effect rather than to the presence of negatively charged anionic groups (COO^-). In other words, the polymer molecules of CAE by themselves on the surface of cement would hinder from flocculating into large and irregular agglomerates of cement particles. This mechanism would be in agreement with the relatively small number of negative anionic groups (COO^-) in the CAE copolymer in comparison with those present as SO_3^- in the SMF and SNF polymers (Fig. 1).

2.2 LABORATORY TESTS ON CONCRETE TECHNOLOGY

Concrete mixes have been produced in the absence and in the presence of CAE, SMF or SNF polymers as superplasticizing admixtures. In the present section only laboratory tests concerning portland cement mixes will be examined.

Preliminary tests have been carried out to study the effect of the way of addition of superplasticizers on the slump of concrete mix. Table 1 summarizes some typical results concerning concrete mixes, with portland cement content of about 360 Kg/m^3, w/c of about 0.40, natural aggregates, coarse maximum size of 20 mm, percentage of sand in the aggregate of 45%. The superplasticizing effect of SMF or SNF is strongly depending on the way of addition, and a delayed addition of superplasticizer (after 1 min of mixing) appears to be much more effective than an immediate addition (superplasticizer with mixing water).
On the other hand, the effect of CAE polymer does not substantially depend on the way of addition and it performs as well as the SMF or SNF polymers in the delayed addition with a dosage which is much lower (0.30% versus 0.50 or 0.48% respectively).
It is worthwhile noting that the immediate addition is the most practical, safe and easy way to dose the supeplasticizer at the batching plant, since dosing superplasticizer at the work site - corresponding to a delayed addition - consumes too much time and does not allow an accurate control of the final slump and admixture dosage.
All these results together mean that the CAE copolymer is potentially more effective than the SMF or SNF polymers from both a scientific and a practical point of view.
The influence of the polymer type on the slump-loss of superplasticized concrete mix is shown in Fig. 5. Again, the CAE copolymer appears to be more effective than the SMF or SNF polymers (with delayed addition) in reducing the slump-loss of concrete mixes (portland cement content of 350 Kg/m^3, natural aggregates, maximum coarse aggregate of 25 mm, percentage of sand in the aggregate of 42%). Although the different slump-loss would indicate that the cement hydration would be retarded by the CAE copolymer more strongly than by SMF or SNF, the compressive strength of the CAE treated concrete appears to be slightly higher than that of SMF or SNF concrete mixes at early ages and even more at later ages (Fig. 6).
Similar results have been obtained for concrete mixes produced and cured in cold weather (Fig. 7 and 8) as well as for concretes subject to steam curing (Fig. 9).

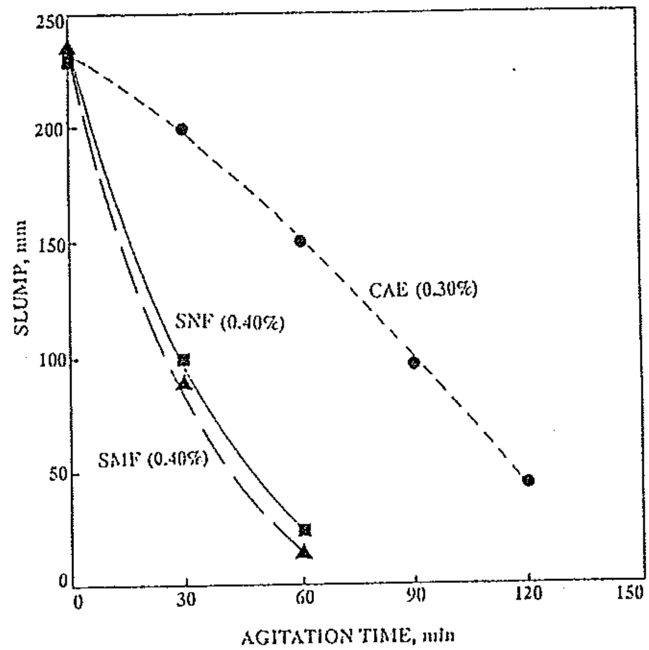


Fig. 5: Slump-loss of superplasticized concrete mixes at 20°C with CAE, SMF or SNF polymers (laboratory tests).

Table 1: Effect of way of addition of CAE, SMF and SNF superplasticizers on the slump of portland cement concrete mixes.

ADMIXTURE			w/c ratio	Slump (mm)
Type	Dosage (%)	Way of Addition*		
CAE	0.30	Immediate	0.39	230
CAE	0.30	Delayed	0.39	235
SMF	0.50	Immediate	0.41	100
SMF	0.50	Delayed	0.41	215
SNF	0.48	Immediate	0.40	100
SNF	0.48	Delayed	0.40	230

* Immediate: admixture with mixing water. Delayed: admixture after 1 min of mixing.

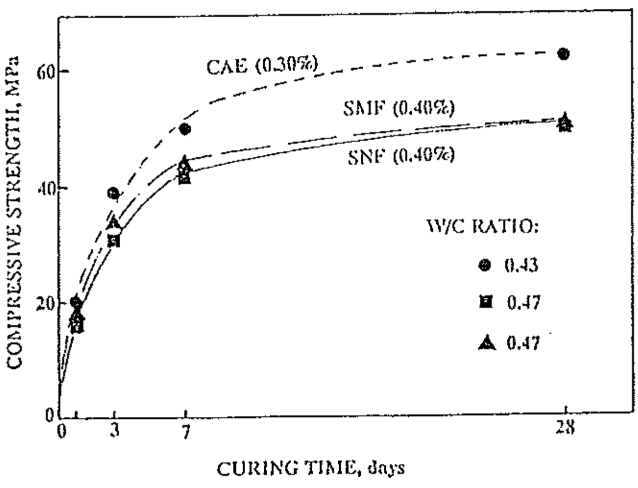


Fig. 6 Compressive strength of superplasticized concrete mixes at 20°C with CAE, SMF or SNF polymers (laboratory tests).

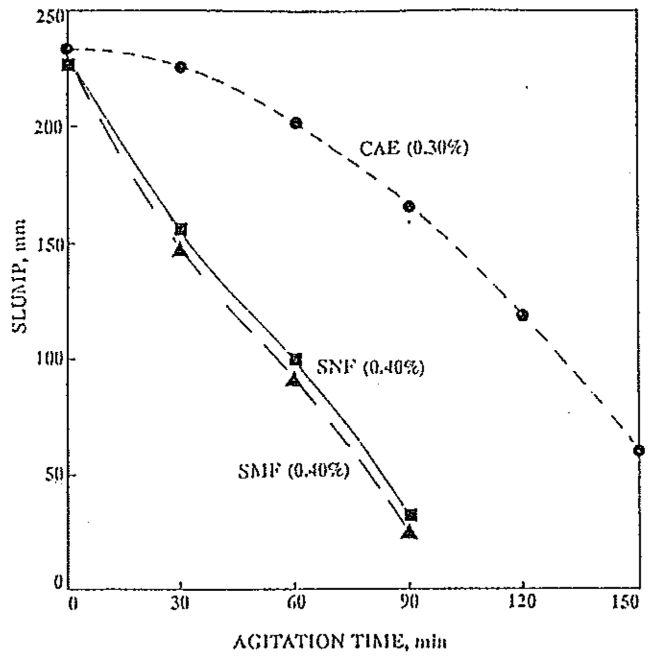


Fig. 7: Slump-loss of superplasticized concrete mixes at 5°C with CAE, SMF or SNF polymers (laboratory tests).

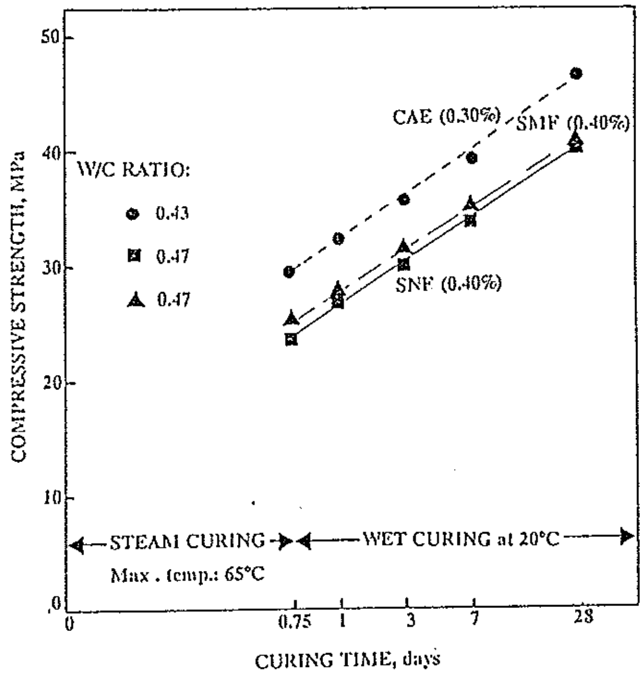


Fig. 9: Compressive strength of steam-cured superplasticized concretes with CAE, SMF or SNF polymers (laboratory tests).

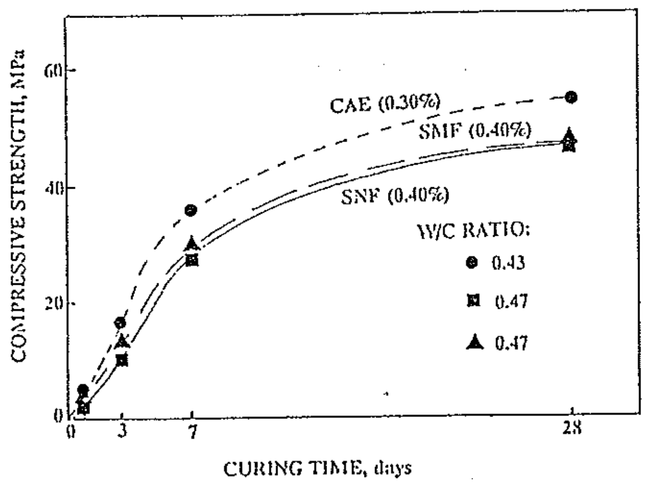


Fig. 8: Compressive strength of superplasticized concrete mixes at 5°C with CAE, SMF or SNF polymers (laboratory tests).

The X-ray diffraction (XRD) analysis (Fig. 10) of portland cement mixes (w/c = 0.40) indicates that ettringite (C3A · 3CaSO4 · 32H2O) whose production is responsible for an appropriate regulation of the setting time in portland cement mixes, is much more promptly formed during the first hours in the presence of CAE copolymer, and could explain why the slump-loss is reduced in the concrete mix containing this admixture (Fig. 5 and 7). On the other hand, the slower formation of Ca(OH)2 at early ages could mean a slightly lower C3S hydration: however this small retarding effect does not affect the concrete compressive strength neither at later nor at earlier ages independently of the curing temperature (Fig. 6, 8 and 9).

Other laboratory tests on the concrete technology including shrinkage, creep and durability [4] - not shown in the present paper for brevity reasons - indicate that all the performances of hardened concrete with CAE copolymer and SMF or SNF polymers are substantially the same, provided that the concrete mix compositions (and in particular w/c and aggregate/cement ratios) are the same. This is in agreement with the scanning electron microscopy (SEM) analysis which demonstrated that the morphology of hydrated cement particles is not changed when SMF or SNF superplasticizers are replaced by the CAE polymer in a given cement system [2].

2.3 FIELD TESTS ON CONCRETE TRANSPORTATION

Concrete batches (5 m^3) with the same mix proportions as those adopted for the laboratory tests, with CAE copolymer (0.30%) and SNF polymer (0.40%), have been manufactured in a batching plant of ready mix concrete company and then transported by truck-mixer for at least 3.5 hours at different temperatures.

In the present paper only the field test results of slump-loss (Fig. 11) and compressive strength (Fig. 12) at a temperature of 21°C will be discussed in order to compare them with the results of the correspon-

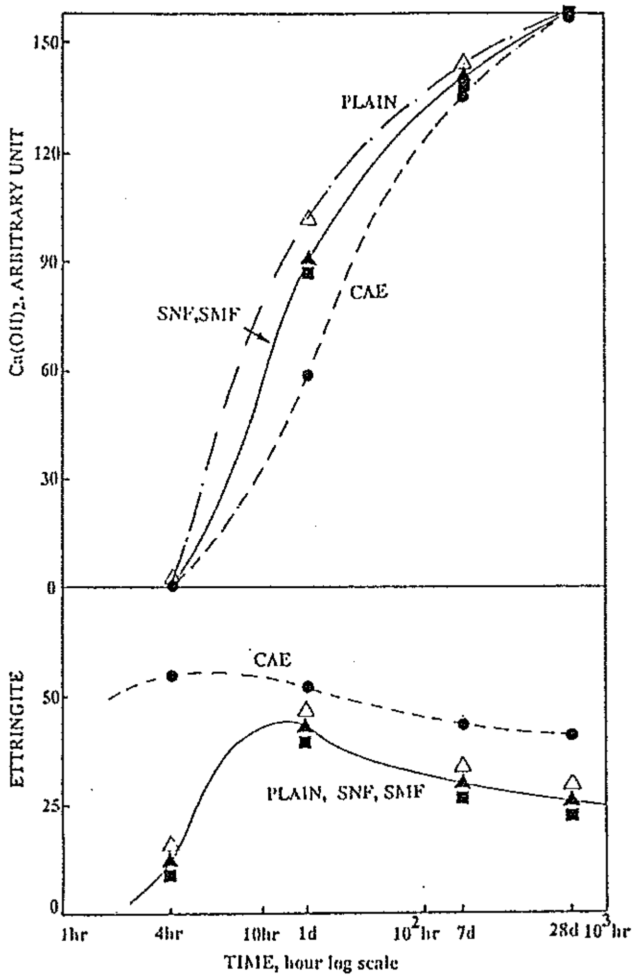


Fig. 10: XRD semiquantitative results for ettringite and $Ca(OH)_2$ production in portland cement pastes with or without CAE, SMF and SNF.

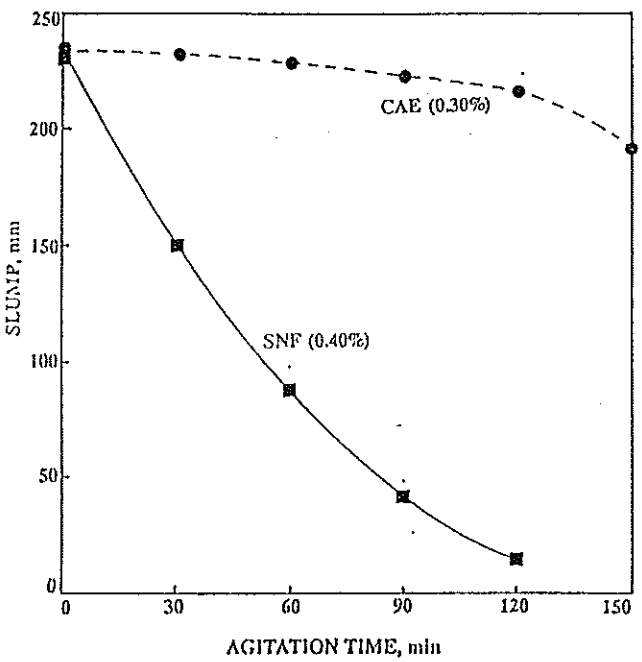


Fig. 11: Slump-loss of ready-mixed concretes with CAE or SNF superplasticizers at 21°C (field tests).

ding mixes (Fig. 5 and 6) examined in laboratory at approximately the same temperature (20°C). In order to make this comparison less favourable for the CAE copolymer, a delayed addition of superplasticizers has been adopted even for the field tests, since this way of addition favours the SNF performance rather than that of CAE copolymer (Table 1).

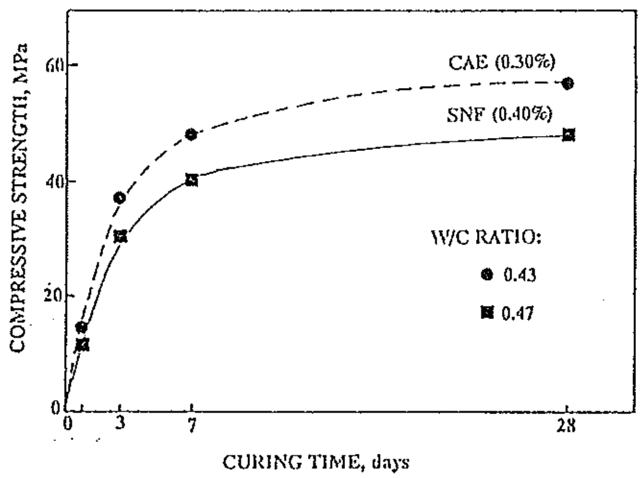


Fig. 12: Compressive strength of ready-mixed concretes with CAE or SNF superplasticizers cured at 21°C.

The slump-loss behaviour of a concrete mix on a small scale (about 0.03 m^3), as that adopted for the laboratory tests (Fig. 5), is generally much more severe than that recorded for the same mix proportion on a large scale when concrete is transported by a truck-mixer. This assumption is confirmed by the comparison of the laboratory results (Fig. 5) and field tests (Fig. 11). Moreover, the slump-loss curves of Fig. 11 indicate that by using the CAE superplasticizer (0.30%) a zero slump-loss concrete mix can be produced for at least 2 hours of transportation, whereas in the presence of SNF (0.40%) the slump-loss is more than 100 mm after 1 hour and about 200 mm after 2 hours. Different dosages of CAE superplasticizer - in the range of 0.2 to 0.4% - should be adjusted to obtain similar slump-loss performances at different temperatures - in the range of 5 to 40°C - and with cements of different reactivity.

Figure 12 shows that compressive strengths of concrete with CAE appear to be higher than those of SNF superplasticized concrete, because of the lower w/c ratio (0.43 versus 0.47) at equal initial slump (230 mm). The difference in the compressive strength is smaller at early ages probably because the early C_3S hydration is slightly retarded more by the CAE copolymer than by the SNF polymer (Fig. 10). Compressive strength values of the ready-mixed concrete specimens (Fig. 12) appear to be lower than those of the corresponding mixes manufactured in laboratory particularly at later ages (Fig. 6). Although a reasonable explanation of this discrepancy has not yet been found, it is confirmed that the CAE copolymer performs better than the SNF polymer as far as the concrete strength is concerned even with a lower dosage (0.30% versus 0.40) and initial equal slump.

3.0 CONCLUSIONS

A new superplasticizer based on the CAE copolymer has been developed and studied in comparison with other polymers (SMF or SNF) usually utilized to manufacture superplasticizers.

The CAE copolymer performs better than the SMF or SNF polymers even with a lower dosage (0.30% versus 0.40% as dry product by weight of cement) because it reduces significantly the slump-loss, which can be completely avoided during the transportation from the batching plant to the work site for at least 2 hours, provided that the proper dosage is adjusted (0.2 - 0.4%) as a function of the cement reactivity and environment temperature.

This is very important from a practical point of view because the practice of redosing the concrete with water above and beyond that required in the mix design can be avoided. Therefore, the properties of the hardened concrete which depend on the w/c ratio (strength, durability,abrasion resistance, etc.) are not lowered as those of retempered concretes.

The superplasticizing action of the CAE polymer does not appear to be dependent on the electrostatic repulsion of cement particles as it occurs for the SMF and SNF polymer. The adsorption of the CAE copolymer on the surface of cement particles seems by itself to be responsible for the dispersion of the cement grains and then for the fluidizing effect.

The slump-loss behaviour of the CAE polymer seems to be related to a more promptly ettringite formation and then to a more effective set regulation of the cement mix.

In the presence of CAE superplasticizer higher strengths can be obtained at equal initial slump level for concretes cured at different temperatures: from cold weather curing (5°C) to steam-curing. If the comparison is done at the time of placing, the CAE superplasticized concrete appears to be more flowable (for the lower slump-loss) and stonger (for the lower w/c ratio) than the corresponding concrete mixes with the SMF or SNF based admixtures.

4.0 ACKNOWLEDGMENTS

The Authors are very grateful to Dr. G. Squinzi (Mapei Group) for the financial support and the encouraging enthusiasm given to the research project, as well as to Mr. A. Borsoi (Enco), Mr. P. Clemente and Mr. D. Salviani (Mapei) for the technical assistance in the experimental work.

5.0 REFERENCES

[1] Asakura A. - Yoshida H. - Nakae H.
"Influence of superplasticizer on fluidity of fresh cement paste with different clinker phase composition "Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, India, Vol IV, Theme III, pg 570-576, 1992.

[2] Cerulli T. - Ferrari G. - Collepardi M.
Unpublished results.

[3] Collepardi M. Ramachandran V.S.
"Effect od Admixtures", Proceedings of the 9th International Congress on the Chemistry of Cement,New Delhi, India, Vol. 1, Theme III D, pg. 529-570, 1992.

[4] Coppola L. - Pistolesi C. - Collepardi. M.
Unpublished results.

[5] Fujiu A. - Tanaka H. - Iizuka M.
"Slump Control by Reactive Polymer Dispersant", Rev. 39th General Meeting, Cement Association, pg. 72-73, Japan, 1985.

[6] Fukuda M. - Mizunuma T. - Izumi T. - Iizuka M. - Hisaka M.M.
"Slump Control and Properties of Concrete with a New Superplasticizer I: Laboratory Studies and Test Methods", Proceedings of the Intern. RILEM Symposium on "Admixtures for Concrete. Improvement of Properties", pg. 10-19, Barcelona, Spain, 1990.

[7] Mitsui K. - Kasami H. - Yoshiota Y. - Kinoshita M..
Properties of High Strength Concrete with Silica Fume Using High Range Water Reducer of Slump Retaining Type" in "Superplasticizers and other Admixtures", Amer. Concr. Inst. SP-119, pg. 79-97, 1989.

[8] Sugrue S..
"Prediction and controlling colloid suspension stability using electrophoretic mobility and particle size measurements", International Laboratory, pg 33-37, 1992.

[9] Yamakawa G. - Kishtiani K. - Fukushi I. - Kuroha K.
"Slump Control Properties of Concrete with a New Superplasticizer. II: High strength in Situ Concrete Work at Hikariga-Oka Housing Project", Proceedings of the Intern. RILEM Symposium on "Admixtures for Concrete. Improvement of Properties", pg. 94-105, Barcelona, Spain, 1990.