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Admixtures Used to Enhance Placing Characteristics of Concrete

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Abstract

Placing characteristics of concrete can be enhanced by using plasticizing and superplasticizing admixtures without any change in the water–cement ratio with respect to the plain mixture. The main ingredients used in superplasticizers are based on sulfonated melamine formaldehyde (SMF) condensate or naphthalene formaldehyde (SNF) condensate. More recently, a new family of products, based on acrylic polymers (AP), has been proposed. These polymers are more effective than those based on SMF or SNF in terms of lower base water–cement ratio at a given slump and lower slump loss. Moreover, the effectiveness of the AP-based superplasticizers does not depend significantly on the mode of addition, whereas the slump level of concrete mixes with SMF- and SNF-based admixtures is much higher with a delayed addition of superplasticizer with respect to that of mixing water. The dispersion of cement particles responsible for the fluidity increase, caused by the superplasticizer addition, is not necessarily related to the electrostatic repulsion associated with zeta potential measurements, as it was found for SMF- and SNF-based admixtures. For the AP-based superplasticizers, the polymer adsorption, rather than the electrostatic repulsion, is responsible for the dispersion of large agglomerates of cement particles into smaller ones, which results in a remarkable increase in the fluidity of cement mixes. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: admixtures, concrete, superplasticizer, acrylic polymers, sulfonated melamine formaldehyde, sulfonated naphthalene formaldehyde.

INTRODUCTION

Plasticizers and superplasticizers can be used in concrete mixtures for three different purposes or a combination of these[1]:

1. to increase workability without changing the mix composition in order enhance placing characteristics of concrete (Fig. 1A).
2. to reduce the mixing water and the water–cement ratio (w/c) in order to increase strength and improve durability at a given workability (Fig. 1B);
3. to reduce both water and cement at a given workability in order to save cement and reduce creep, shrinkage and thermal strains caused by heat of cement hydration (Fig. 1C).

In the present report, superplasticizers will be examined primarily as admixtures to increase the workability level (Fig. 1A).

The main difference between plasticizers and superplasticizers is in the extent rather than in the type of performances. The slump increase at a given mix composition is about 150–200 mm for the latter and about 50–70 mm for the former. On the other hand, a superplasticizer is capable of reducing water requirements at a given slump by about 20–30%, whereas a plasticizer can reduce water contents by only about 5–12%.

Further reductions in mixing water or higher slump increases can be obtained by using plasticizers at higher dosages (as those normally adopted for superplasticizers), but this may result in adverse effects on setting, air volume and strength of concrete. Therefore, from a practical point of view, the main difference between plasticizers and superplasticizers is in the optimum dosage, which is about 0.2–0.4% by mass of cement for plasticizers and 1–2% for superplasticizers. The actual dosage of the active ingredients in both these admixtures is really much lower than the above figures since they are generally available in a form of 30–40% aqueous solution in order to facilitate accurate, reliable and automatic dispensing at the batching plant.

COMPOSITION OF PLASTICIZERS AND SUPERPLASTICIZERS

From a compositional point of view plasticizers and superplasticizers may be quite different (Table 1). The main ingredients in the superplasticizers are synthetic water-soluble polymers, such as sulfonated melamine formaldehyde (SMF) condensate or sulfonated naphthalene formaldehyde (SNF) condensate. Alternative water soluble synthetic polymers have been recently proposed[2–11] to reduce the slump-loss drawback, which can partly or completely cancel the initial technical advantage associated with the use of superplasticizers (low w/c ratio or high slump level). In the absence of these new low slump loss superplasticizing admixtures—based on acrylic polymers (AP)—the slump loss problem has been approached by using retarding admixtures as secondary ingredients to partly compensate for the stiffening process of the fresh concrete before its placement.[1] In some cases, chloride-free inorganic salts are used as secondary ingredients to compensate for the retarding effect associated with heavily dosed superplasticizer systems (2%).

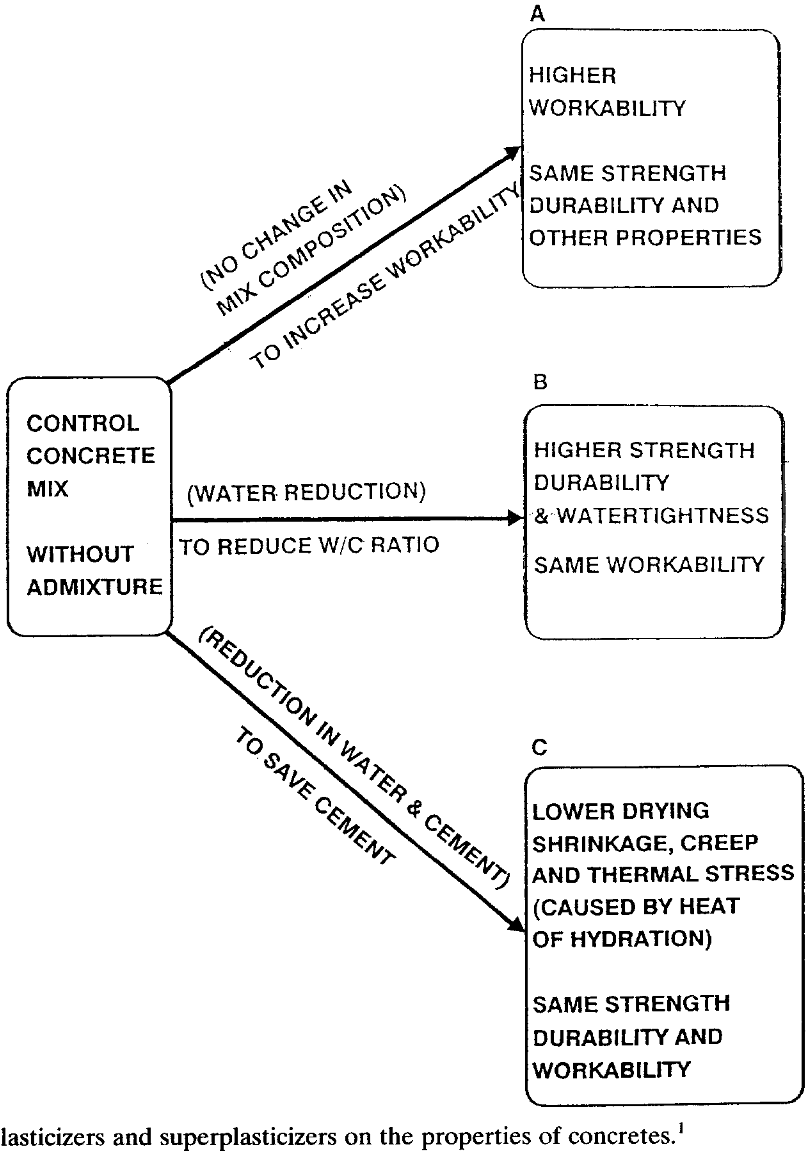


Fig. 1. The effect of plasticizers and superplasticizers on the properties of concretes.[1]

Table 1. Main and secondary ingredients in plasticizing and superplasticizing admixtures[2]

Superplasticizers		*Plasticizers*	
Main ingredients	*Secondary ingredients*	*Main ingredients*	*Secondary ingredients*
SNF	MLS	LS/MLS	TEA
SMF	Retarders	HC	Inorganic salts
AP	Inorganic salts	CH	Defoaming agents
Others	TEA	Others	Anti-bacterial products

SMF, sulfonated melamine formaldehyde; SNF, sulfonated naphthalene formaldehyde; AP, acrylic polymers; MLS, modified form; TEA, triethanolamine; LS, lignosulfonic acid; HC, hydroxycarboxylic acids; CH, carbohydrates.

The main ingredients used in the manufacture of plasticizers are organic products and can be divided into four groups. The first contains salts of lignosulfonic (LS) acid, which can also be used as an important ingredient of superplasticizers when available in a modified form (MLS), and consists mainly of a de-sugarized product with reduced retarding effects. The second group contains salts of hydroxycarboxylic acids (HC). The carbohydrates (CH) belong to the third group, whereas the fourth group contains miscellaneous compounds such as glycerol, polyvinyl alcohol, etc.[1] Other secondary ingredients in plasticizers may be accelerating products such as triethanolamine (TEA), or calcium and sodium of inorganic acids, as well as defoaming agents, anti-bacterial and anti-fungal materials to avoid gas development caused by the transformation of the organic main ingredients.

Figure 2 shows the chemical structure of the most important sulfonated (SNF, SMF, AS, LS) and acrylic polymers — such as copolymers of carboxylic acrylic acids (CAE), polycarboxylate ester (PC) and cross-linked acrylic polymer (CLAP) — used as active ingredients of superplasticizing admixtures.

ACTION MECHANISM OF SUPERPLASTICIZERS

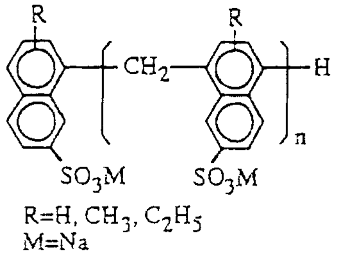
Superplasticizers cause dispersion into smaller agglomerates of cement particles, which predominate in the cement paste of the concrete mix. Because of the dispersion effect, there is a fluidity increase in the cement mixture. In the past, the dispersion effect was ascribed to the development of the electrostatic (negative) charge on the cement particles.[12,13] The attractive forces existing among cement particles that cause agglomeration would be neutralized by the adsorption of anionic polymers, such as SNF or SMF, by the presence of SO_3^- groups on the surface of cement particles. The dispersion of cement particles would be related to the electrical repulsion produced by the adsorption of negatively charged groups.

Additional experimental results have not confirmed this mechanism for the superplasticizing action of the acrylic polymers.[3,8–11] To study the dispersion and superplasticizing effects of acrylic and sulfonated polymers, the fluidity of Portland cement mortar mixes with w/c of 0.40 and sand/cement of 3 was measured (at 5 min) in the absence or in the presence of different dosages of CAE or SNF admixtures (0.0–0.6% of dry polymer to mass of cement). Figure 3 shows the flow table measurements of these mortars and indicates that the CAE copolymer performs much more effectively than the SNF polymer.

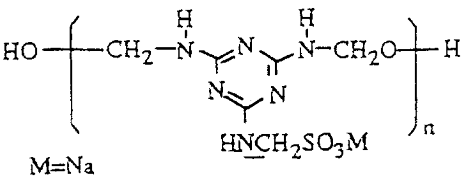
The aqueous phase of Portland cement pastes (w/c = 2) was analyzed by the total organic content (TOC) technique[14] to determine the residual concentration of polymer after 5 min of agitation, so that the content of admixture adsorbed onto cement could be calculated. Figure 4 shows the percentage of polymer adsorbed as a function of the admixture dosage expressed as the percentage of dry polymer by mass of cement. The adsorption of CAE copolymer (about 85%) appears to be higher than that recorded for the SNF polymer (75%). Figure 5 shows the results of zeta potential measurements on the same Portland cement pastes determined by a multi-angle electrophoretic light scattering (ELS) technique.[15] The zeta potential of cement particles treated with CAE appeared to be much lower than those recorded in the presence of SNF. In particular, when 0.3% of CAE by mass of cement was used, the cement particles appeared to be electrically neutral even though the corresponding mortar mix, with the same percentage of admixture (0.3%), was much more fluid than the plain mix and that with the SNF polymer (Fig. 3).

All these results indicate that the dispersion of cement particles, responsible for the fluidity increase caused by superplasticizer, is not necessarily related to the electrostatic repulsion associated with zeta potential measurements. It would seem that, at least for the CAE admixture, the polymer adsorption (Fig. 4), rather than the electrostatic repulsion (Fig. 5), is responsible for the dispersion of large agglomerates of cement particles into smaller ones and for the remarkable increase in the fluidity (Fig. 3) of cement mixes.

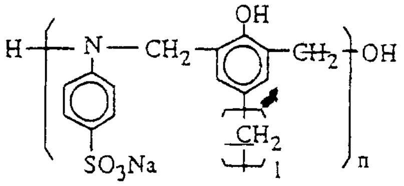
The dispersion mechanism performed by the CAE polymer could be related to a steric hindrance effect rather than to the presence of negatively charged anionic groups (COO^-). In other words, the polymer molecules of CAE on the surface of cement might themselves hinder flocculation into large and irregular agglomer-



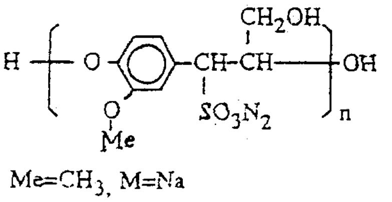
SNF
(Sulfonated naphtalene formaldehyde)



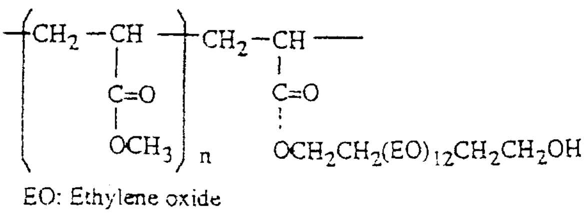
SMF
(Sulfonated melamine formaldehyde)



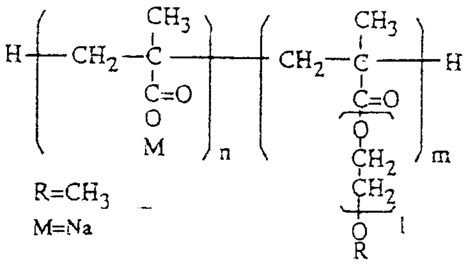
AS
(Amino-sulfonate polymer)



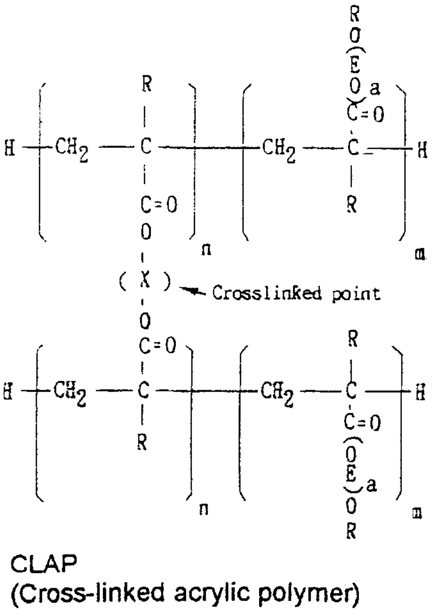
LS
(Lignosulfonate)



PC
(Polycarboxylate ester)



CAE
(Copolymer of carboxylic acrylic acid with acrylic ester)



CLAP
(Cross-linked acrylic polymer)

Fig. 2. Chemical structure of sulfonated and acrylic polymers.[3,10,11]

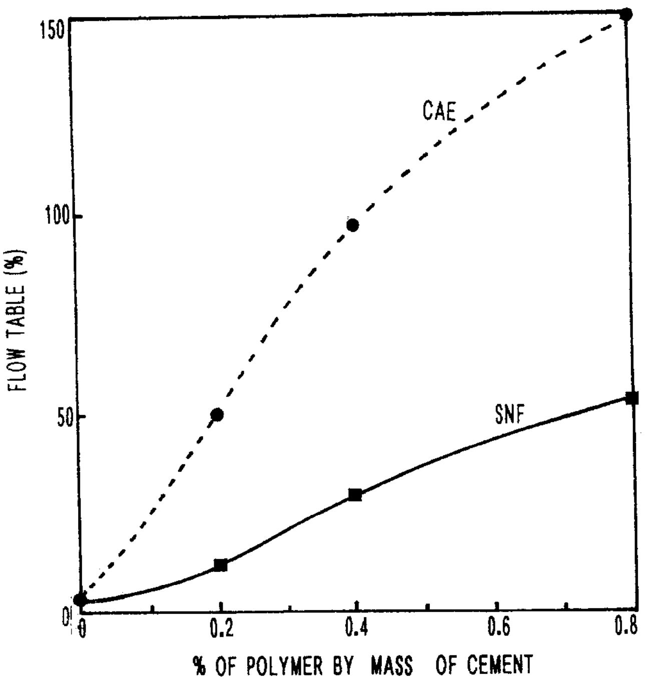


Fig. 3. Influence of CAE or SNF polymers on the fluidity of portland cement mortar mixes with w/c = 0.4.[3]

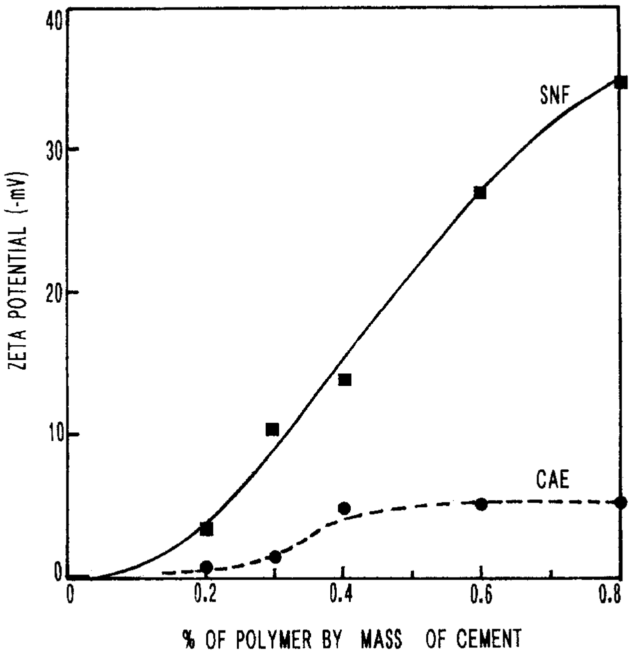


Fig. 5. Zeta potential of CAE or SNF cement pastes as a function of polymer dosage.[3]

ates of cement particles.[3] This mechanism would be in agreement with the relatively smaller 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. 2).

The results by Uchikawa[10] and Tanaka *et al.*[11] indicate that the steric hindrance effect should be taken into account to explain the action mechanism of the AP-based superplasticizers, whereas the electrostatic repulsion mechanism is the predominating effect for sulfonated polymer-based (SMF, SNF, AS) superplasticizers. Moreover, additional mechanisms of the superplasticizing action include dispersion of cement particles by reduction in surface tension of mixing water[10] and a decrease in friction resistance because of the line-up of linear polymers along the concrete flow direction and lubrication properties produced by low molecular weight polymers.[11]

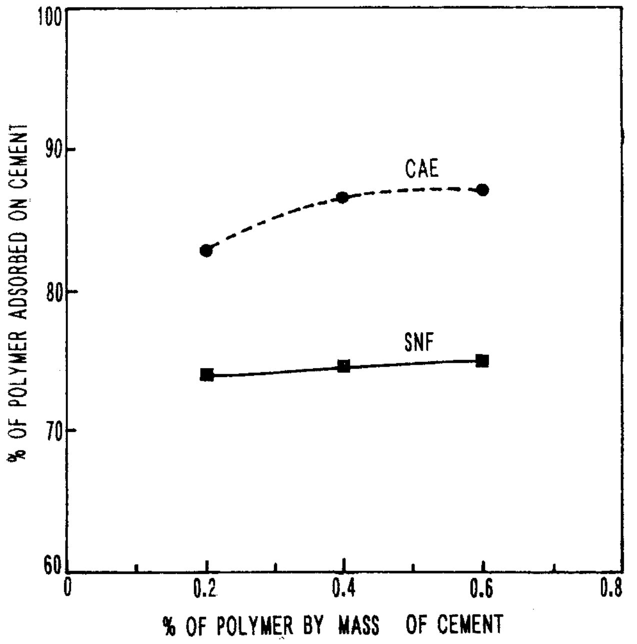


Fig. 4. Adsorption of CAE or SNF on cement as a function of polymer dosage.[3]

According to Tanaka *et al.*[11] the segregation resistance of superplasticized concrete mixtures is primarily caused by the coagulation effect of higher molecular weight polymers—from hundreds of thousands to millions—to bridge different cement particles. This could explain why AP-based superplasticizers, with higher molecular weight with respect to SMF or SNF, perform better in terms of higher segregation resistance in fresh concrete mixtures.

METHOD OF ADDITION

The SMF- or SNF-based superplasticizers are available as a 40% aqueous solution. Both are able to transform a no-slump concrete into a self-leveling mix with a slump increase of about

200 mm. However, the method of addition of these superplasticizers affects the slump-increase effect. Figure 6[9] shows that an immediate addition procedure (SNF superplasticizer with gauging water) produced a less workable mix compared with delayed addition of the same superplasticizers (after an initial mixing period of 1 min).

The influence of the time of addition on the effect of superplasticizer has been ascribed to the different capabilities of SMF or SNF polymer molecules to be adsorbed on anhydrous or hydrated cement particles.[16] For instance, a preliminary treatment of cement, even with a small amount of water (1–2%), produces superplasticized concrete mixes that, independently of the method of addition of the superplasticizer, always perform as well as the best concrete produced by delayed addition.[17] This effect seems to be related to the production of an ettringite coating on the surface of cement particles during the preliminary water treatment. It seems that addition of superplasticizers with mixing water causes a strong incorporation of the polymer molecules into the C_3A – gypsum system, and leaves only small amounts of polymer for dispersion of C_3S and C_2S. Consequently, the adsorption of SMF or SNF polymer molecules on the prehydrated cement surface is reduced and the subsequent dispersing action appears to be much more effective than that recorded in the absence of the preliminary water treatment.

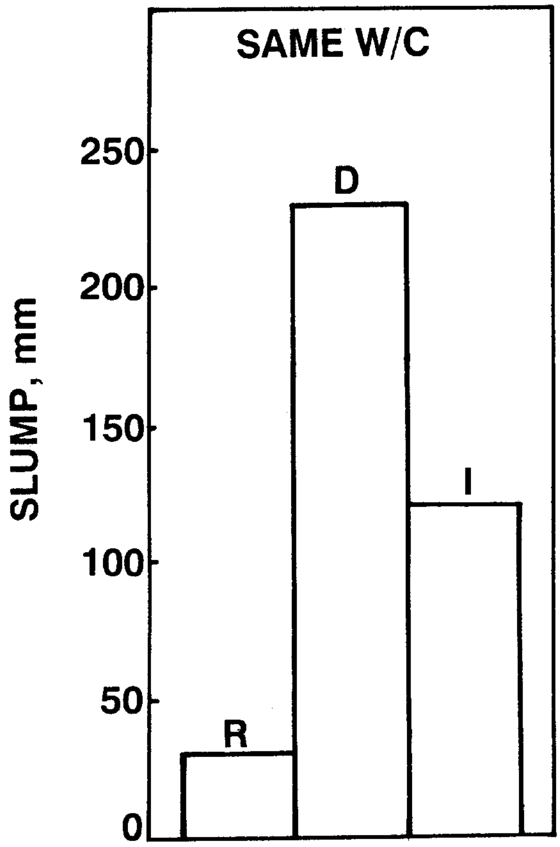


Fig. 6. Effect of the SNF superplasticizer (0.45% as dry polymer) addition procedure on the change of properties with respect to the reference mix (w/c = 0.45). R, reference mix (without superplasticizer); D, superplasticized mix (delayed addition); I, superplasticized mix (immediate addition).

A superplasticizer that could perform independently of the method of addition would be much appreciated at the batching plant of ready-mixed or precast concrete, in order to reduce the variability in the slump of fresh mix or in the strength of hardened concrete caused by a change in the procedure of superplasticizer addition. The acrylic polymer-based superplasticizers seem to be very interesting admixtures because they perform without depending on the addition procedure. Table 2 shows the slump of concrete mixes as a function of the superplasticizer procedure addition (delayed or immediate) when SMF- and SNF- or CAE-based polymers are used (Table 3).[3]

Results by Uchikawa[10] confirm that the NSF polymer is adsorbed more, particularly on the C_3A hydration products, when the immediate addition procedure is adopted. Moreover, according to Uchikawa,[10] the superplasticizing effect is improved with a delayed NSF-polymer addition because of the lower adsorption of the polymer on the C_3A hydration products; on the other hand, the adsorption of the PC acrylic polymer (Fig. 2) does not depend on the method of addition (immediate or delayed).

SLUMP LOSS

The slump loss problem appears to be even more serious than that related to the different

Table 2. Comparitive costs of superplasticizers as a percentage compared with 1 kg of dry acrylic polmer

Concentration of aqueous solution (%)	*Cost of aqueous solution*	*Cost of dry polymer*
30% AP	30	100
40% SMF	32	80
40% SNF	16	40

SMF, sulfonated melamine formaldehyde; SNF, sulfonated naphthalene formaldehyde; AP, acrylic polymers.

Table 3. Effect of addition of mono-component copolymer (CAE), sulfonated melamine formaldehyde (SMF) and sulfonated naphthalene formaldehyde (SNF) superplasticizers on the slump of Portland cement concrete mixes[3]

Admixture			*Concrete mixture*	
Type	*Dosage (%)*	*Mode of addition*[a]	*W/C ratio*	*Slump (mm)*
CAE	0.30	Immediate	0.39	230
CAE	0.30	Delayed	0.39	235
SMF	0.30	Immediate	0.41	100
SMF	0.30	Delayed	0.41	215
SNF	0.30	Immediate	0.40	100
SNF	0.30	Delayed	0.40	230

[a] Immediate: admixture with mixing water. Delayed: admixture after 1 min of mixing.

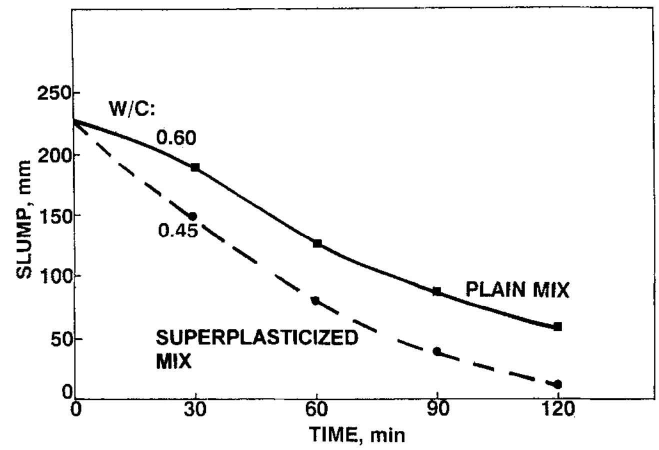


Fig. 7. Slump-loss at 20°C for plain and superplasticized mix at the same initial slump. Superplasticizer: 0.4% as dry SNF polymer by weight of cement.[8]

performances caused by the superplasticizer addition procedure. When a concrete mix must be transported for a long peroid, particularly in hot weather, it should keep as moist as possible in the initial slump level to avoid redosing the concrete with water above and beyond that required in the mix design. Results of investigations of retempered concrete indicate that many of the properties of the hardened concrete (strength, durability, abrasion resistance, etc.) are significantly affected, since retempered concrete does not perform as well as concrete that has not been retempered.[18] However, slump loss is un-avoidable because of the intrinsic requirement for cement mixes, which should set and harden in a relatively short time. Therefore, a right and proper compromise would be a zero-slump-loss concrete mix for about 1 hour. By using traditional superplasticizers based on SNF or SMF polymers it is not easy to achieve this target, because in general, slump loss is higher in superplasticized concrete with respect to the corresponding plain mix at a given initial slump (Fig. 7). The lower the w/c, the higher the slump loss for the same initial slump level. It seems that the lower w/c in superplasticized concrete and the consequent lower distance among cement particles causes a more significant slump loss when the same amount of water is lost through evaporation or by reaction with cement during the transportation time (Fig. 8).

Several methods have been adopted to control the rate of slump loss. One method it to add the superplasticizer at the point of discharge but there are some practical problems associated with this approach. For instance, the concrete into the truck-mixer before the superplasticizer addition would be too stiff at the placement when a high-quality concrete (with low w/c) is produced. Moreover, dosing the superplasticizer at the work site consumes too much time and does not allow an accurate control of the final slump and admixture dosage.

Other methods to control slump loss include adding a higher than normal dosage of superplasticizer or using some type of retarding admixture in the formulation. However, there are some limits of this approach, because sometimes the final effect is to produce concrete with an unacceptably low early strength or to aggravate slump loss more seriously. For instance, slump loss accompanied by a surprisingly quick set may be recorded by using retarders such as sugar, sucrose, corn syrup or calcium lignosulfonate.[19] The cement content, as well as the chemical and mineralogical composition of cement, play an important role in determining

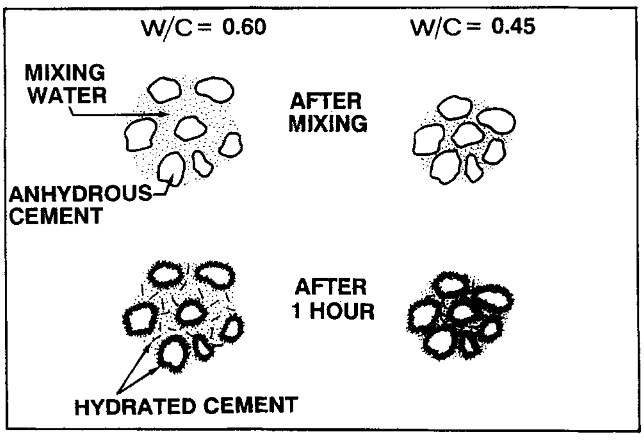


Fig. 8. Schematic picture of cement paste in a plain ($w/c = 0.60$) and superplasticized concrete ($w/c = 0.45$).[8]

such a singular slump loss, although the detailed mechanism is not clear. It seems that the content of C_3A, gypsum and alkali, as well as the form of calcium sulfate used as set regulator, can affect the rate of slump-loss.

Also redosing the superplasticizer at different intervals of time has been suggested[12] to reduce slump-loss, but this method appears to be not always easy to adopt in practice. Moreover, the total dosage of superplasticizer, as well as the relative cost, cannot be kept under control according to the given plan.

Therefore a superplasticizer is required, which by itself is capable of maintaining the slump for a long period of time independently of the temperature or the type and content of cement. Fujiu *et al.*[4] have developed a polymer (with ester, amides and acid anhydrides as functional groups), which by itself is not soluble in mixing water, but under the alkaline environment formed in the aqueous phase in contact with cement, is slowly transformed into an aqueous soluble product that has a superplasticizing effect. The mechanism of this method is based on the principle that the effectiveness of superplasticizers is significantly reduced by rapid adsorption in the early periods of cement hydration.

Fukuda *et al.*[5] and Yamakawa *et al.*[7] have examined the slump loss performance of a commercial superplasticizer that has two different components: a SNF polymer that acts immediately as a dispersing agent and a reactive polymer (in the form of an insoluble precursor) as a slump loss reducer. The OH^- anions, generated by cement hydration, attack the insoluble reactive polymer. This is transformed into a water-soluble dispersant that contributes to the stabilization of the dispersion and reduces slump loss. The slump loss is negligible up to 60 min (Fig. 9) with a dosage of superplasticizer in the range of 1.5–3.5% (by mass of cement), which appears to be much higher than the normal dosage (1%). Because of the negligible slump loss, both the required workability at the work site (160–200 mm) and the designed 28-day compressive strength (43 or 54 MPa) can be attained with a very small variation in quality (Fig. 10) since retempering of concrete with additional water on the work site is avoided. This means that ready-mixed concrete can be

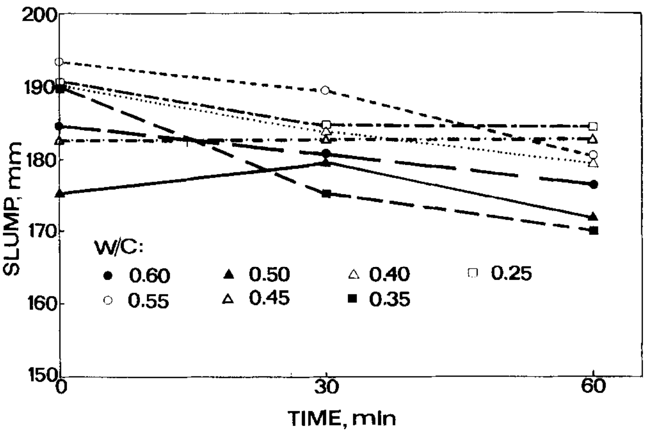


Fig. 9. Slump-loss curves with a bicomponent superplasticizer.[5]

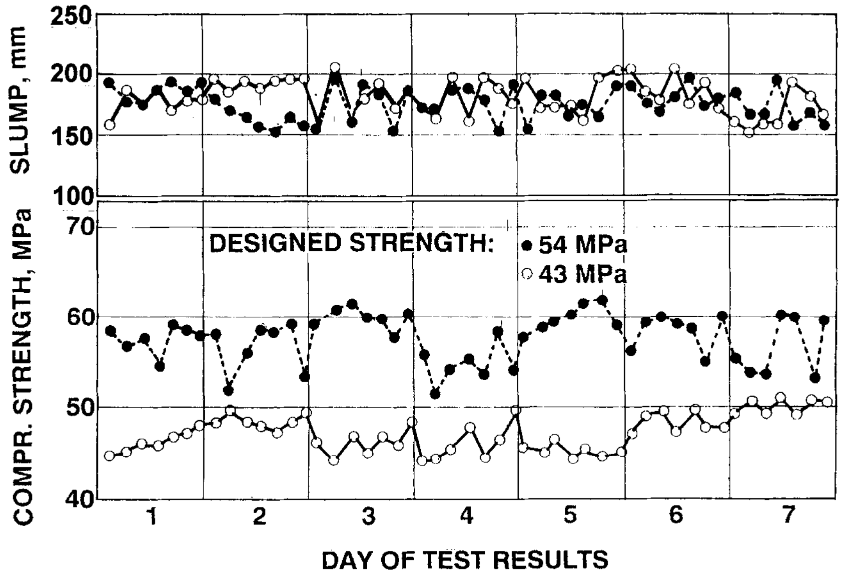


Fig. 10. Slump and 28-day compressive strength of 49 concrete batches produced in 7 different days.[7]

manufactured under quality controls that approach those adopted in the industrial process of other construction materials such as steel, polymer, ceramics, etc.

Mitsui *et al.*[6] examined the performance of a bi-component superplasticizer, based on the combined action of a SNF polymer as a dispersing agent and a copolymer (with sulfonic and carboxylic functional groups) as slump loss reducer. The authors have found negligible slump loss at temperatures in the range of 10–30°C up to 60 min with a dosage of superplasticizer of about 1–2% in concrete without silica fume and 2.5–5% in the presence of silica fume.

Collepardi *et al.*[3] studied the effects of a water soluble mono-component copolymer (CAE) on the properties of ready-mixed concrete mixtures. This superplasticizer acts both as an immediate dispersant and as a slump loss reducing agent. The concentration of the active CAE ingredient in the aqueous phase of this superplasticizer is lower than that of traditional NSF based superplasticizer (30% versus 40%). However, although both of these superplasticizers have been used at the same dosage (1% by mass of cement), and therefore with different contents of active polymer (0.30% s/s versus 0.40% s/s), the CAE-based superplasticizer was more effective than that based on SNF for water-reducing capability (w/c = 0.43 versus 0.47) as well as for maintenance of initial slump level (Fig. 11). The compressive strength of the CAE superplasticized concrete was higher than that of the corresponding concrete with the SNF-based superplasticizer at early and especially at longer ages, because of the lower w/c: the retarding effect of the CAE superplasticizer, which was beneficial to the reduction in slump loss, did not reduce the 1-day compressive strength with respect to the concrete that contained the less retarding SNF superplasticizer (Fig. 11B).

Tanaka *et al.*[11] studied the effect of an AP-based superplasticizer on the slump-loss of a concrete mixture. This superplasticizer is a partially cross-linked copolymer of acrylic acid and polyethylene glycol mono-alkyl ether (Fig. 2). According to Tanaka and co-workers the cross-linked polymer is hydrolyzed by the alkaline water phase of the cement paste and than converted into an acrylic polymer. Both the steric hindrance effect and the electrical repulsive force caused by the negative carboxylic groups are responsible for the dispersion of cement particles and the fluidizing action of the admixture. The low slump-loss effect of this superplasticizer should be related with the protruding side chains of the acrylic polymer, which would prolong the dispersion of hydrated cement particles through a steric hindrance effect.

CONCLUSIONS

Superplasticizers are able to enhance the placing characteristics of concrete mixtures by increasing the workability level at a given w/c. Therefore they allow easier placement of concrete mixtures, even with low w/c when required for strength or durability reasons.

Two drawbacks of superplasticized concrete mixtures can occur when traditional sulfonated polymer-based (SMF and SNF) admixtures are

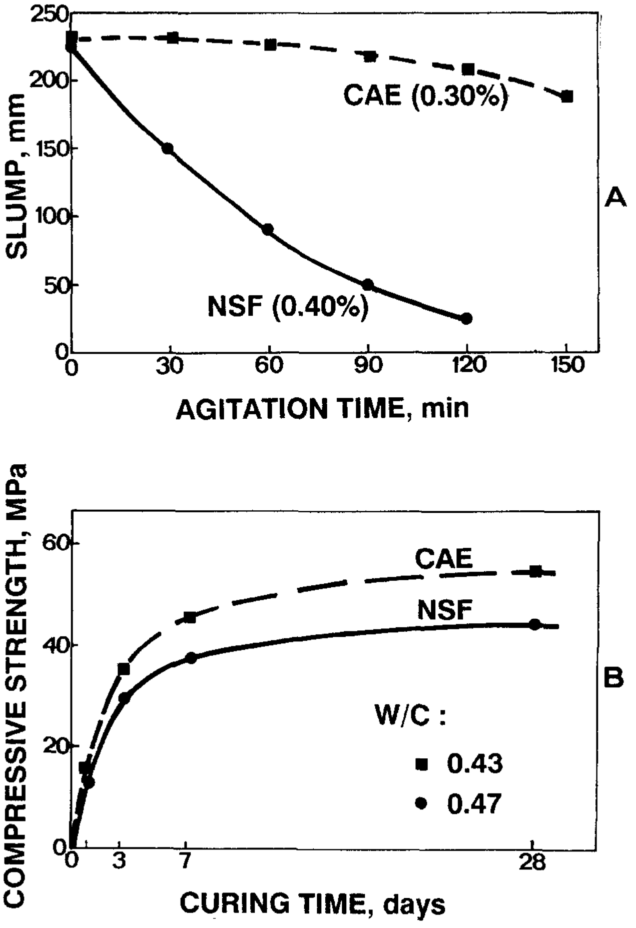


Fig. 11. Slump-loss (A) and compressive strength (B) at 21°C of superplasticized concretes with OPC and CAE or SNF polymer-based admixtures. The figures on the slump-loss curves indicate the percentage of the superplasticizer active ingredient × mass of cement.[8]

used: the effectiveness of the fluidizing action depends on the addition procedure (immediate or delayed); the slump-loss can reduce or cancel the advantage of using these superplasticizers, particularly in hot weather, with long transportation times and reactive cements.

A new family of superplasticizers—all based on acrylic polymers—is available with improved placing characteristics: (i) flowing concretes can be produced at lower w/c with respect to concrete mixtures containing sulfonated superplasticizers; (ii) the effectiveness does not depend on the addition procedure (immediate or delayed); and (iii) the slump-loss is much more reduced with respect to concrete mixes with traditional sulfonated superplasticizers.

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