DEVELOPMENT IN CHEMICAL ADMIXTURES FOR HIGH PERFORMANCE READY MIXED CONCRETE

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ABSTRACT

The development of the most important chemical admixtures for ready mixed concrete is examined in the present paper.

Water reducers, and in particular superplasticizers, are used to produce high stregnth and/or durable concretes exposed to very aggressive environments.

New acrylic polymers are available to manufacture low slump loss ready mixed concrete. Therefore, less strength change should occur with respect to the required level because the addition of extra-water on the job site should be reduced or completely avoided.

More reliable air void systems to produce frost resistant concrete are needed: plastic hallow microspheres instead of air entraining agents could be used provided that more economical materials will be available.

"Extended" or "super" retarders have been developed for re-use of returned plastic concrete or treatment of truck wash water in order to face-up to the environmental concerns.

More research efforts should be devoted in the coming years to produce effective and reliable alkali-aggregate expansion reducers and corrosion inhibitors for reinforced concrete structures exposed to the risk of cracking.

1. INTRODUCTION

Admixtures are ingredients other than water, cement, and aggregate added to the concrete batch during its mixing.

Chemical admixtures are generally used in small amounts and most of them are water soluble or emulsified products. According to this definition chemical admixtures are exclusive of fiber reinforcement, polymer addition, expansive agents, and mineral additions such fly ash, slag and silica fume.

The most important chemical admixtures include water reducers, retarders, accelerators, air-entraining agents, alkali-aggregate reaction inhibitors and corrosion inhibitors.

There has been a continuous development of chemical admixtures as evinced by published literature (1-6) and the relevant activity involves mainly cement and material scientists.

2. WATER REDUCERS

Plasticizers and superplasticizers are chemical admixtures which can be used either to increase the workability of fresh concrete at a given mix composition (Fig. 1/A) or to reduce tha amount of mixing water of concrete for given workability and cement content, so that the water/cement (*w/c*) is reduced (Fig. 1/B). According to a more appropriate terminology, in the latter mode of use these chemical admixtures should be called water reducers.

There is an other mode to use these admixtures, involving reduction of both water and cement, so that workability and strength of the concrete containing admixtures are similar to those of the control concrete (Fig. 1/C). When used in this way, these admixtures act as cement savers and therefore are capable of reducing the drying shrinkage and creep or the heat of hydration, a property that is useful for concreting in hot climates or massive structures.

The main difference between plasticizers and superplasticizers is in the extent rather than in the type of their 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 about 5-12% only.

Since the *w/c* is the most important parameter affecting the main properties of the concrete in service (strength, durability, etc.) more effecting chemical admixtures, which are capable to reduce the *w/c* without sacrificing the mix workability, will be needed in the future in constructions where concrete with high performances characteristics will be required. From this point of view, plasticizers are expected to be progressively replaced by superplasticizers and new synthetic polymers will be tested to attain to cheaper admixtures, improved slump-loss performance, increased water reduction capability.

Special and high performance concretes will be required to attain to:

- high compressive strength (40-70 MPa) or ultra high strength (70-120 MPa);
- high durability against aggressive environments such as in offshore structures, ocean sea floor tunnels;
- special characteristics for repairs or utilization of waste materials and solidification of hazardous materials in cement mixes.

Presently, the most important available superplasticizing admixtures are based on SMF (sulfonated melamine formaldehyde condensate) or SNF (sulfonated naphtalene formaldehyde condensate) in form of a 40% aqueous solution. Both are able to transform a no-slump concrete into a self-levelling mix with a slump increase of about 200 mm. However, slump-loss may reduce the beneficial effect at the time of placing. and this is a practical limit particularly in ready-mixed concrete.

When a concrete mix must be transported for a long time, particularly in hot weather, it should keep as most as possible the initial slump level to avoid the practice of 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 which has not been retempered (7). 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 1-2 hours. 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 the superplasticized concrete with respect to the corresponding plain mix at given initial slump.

Several methods have been adopted to control the rate of slump loss. One method is 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*), should be 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 in this approach, because sometimes the final effect is to produce concrete with un-acceptable low early strength or to aggravate more seriously slump loss. 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 (8). The cement content, as well as the chemical and mineralogical composition of cement, play an important role in determining 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 (1) to reduce slump-loss, but this method appears to be not always easy to be adopted in practice. Moreover, the total dosage of superplasticizer, as well as the relative cost, cannot be kept under control according to a given plan.

Therefore a new superplasticizer is required which by itself is capable to maintain the slump for a long period of time (at least 1-2 hours) independently of the temperature, or the type and content of cement. Some recent developments in this direction will be discussed in the present paper.

Fujiu et al. (9) have developed a polymer (with ester, amides and acid anhidrides as functional groups) which by itself is not soluble in mixing water but, under the alkaline enviroment formed in the aqueous phase in contact with cement, is slowly transformed into an aqueous soluble product having 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. (10) Mitsui et al. (11) and Yamakawa et al. (12) have examined the slump loss performance of a commercial superplasticizer which has two different components: SNF polymer acting immediately as dispersing agent and a reactive polymer (in form of an insoluble precursor) as a slump loss reducer. The OH^- anions generated by cement hydration attack the unsoluble reactive polymer. This is transformed into a water soluble dispersant which contributes to the stabilization of the dispersion and reduces slump loss. The slump loss is negligible up to 60 min (Fig. 2) with dosage of superplasticizer in the range of 1.5-3.5% (by weight 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 very small quality variation (Fig. 3) since retempering of concrete with additional water on the work site is avoided. This means that also ready-mixed concrete can be manufactured under quality controls approaching those adopted in the industrial process of other construction materials such as steel, polymer, ceramics, etc.

Mitsui et al. (11) examined the performance of a bicomponent superplasticizer, based on the combined action of a SNF polymer as 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 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. (13) have studied the effects of a new water soluble monocomponent copolymer (Carboxylated Acrylic Ester or CAE) on the properties of ready-mixed concrete mixtures. This superplasticizer acts as both an immediate dispersant and 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 weight 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 the water reducing capability (*w/c* = 0.43 versus 0.47) as well as for the maintainance of the initial slump level (Fig. 4A). 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 containing the less retarding SNF superplasticizer (Fig. 4B).

Superplasticizers can be used to reduce the amount of mixing water without changing the cement content in order to reduce the *w/c* and therefore to increase strength or improve durability. In such a case, according to a more appropriate terminology, these chemical admixtures should be called high-range water reducers rather than superplasticizers.

Plain, reinforced or prestressed concrete structures in general do not need a level of compressive strength higher than 60-70 MPa, and compressive strength in the range of 30-40 MPa is usually required for many practical purposes in the field of civil engineering. With the available high-range water reducers, even higher levels of strength can be attained because a reduction in the *w/c* up to 0.35-0.40 can be easy realized. Therefore, it does not seem that new and more effective high-range water reducers are needed for this specific purpose, at least in the near future. When, for special purposes, very high strength levels (up to 150 MPa) are required, the combined addition of a high-range water reducer and silica fume appears to be successful in reducing the capillary porosity of the cement matrix to a more significant extent. However, in such a case the most important role is played by the quality of the aggregate or the paste-aggregate interface rather than by the cement matrix porosity.

Even for durability purposes (when concretes resisting to freezing-thawing, sulphate attack, chloride penetration or carbonation must be produced), the available high-range water reducers are capable to reduce the *w/c* up to the lowest level (0.40-0.45) required for instance by American (14) or European (15) specifications. Thus, again, it does seem that more effective high-range water reducers are needed for these purposes.

Perhaps, cement mixes with *w/c* as low as 0.20-0.35 could be useful to produce frost resistant concretes without air-entrainment. However, it has been found that air-entrainment is absolutely required, particulary with low w-c ratios, to produce durable portland cement concretes which are able to resist to the attack of $CaCl_2$ used as de-icing salt independently of the freezing-thawing effect (16).

Superplasticizers can be used to reduce both water and cement so that concrete mixes are produced with the same *w/c* and at the same slump level. In such a case superplasticizers are able to reduce the cement content. Presently, the reduction of cement content by using the available chemical admixtures can be as high as 35%, when higher than normal dosages are adopted such as 2-3% by weight of cement. The reduction of the cement content, apart from the economical reasons, can be required to change all the properties which are improved by increasing the aggregate/cement at a given *w/c*. Thermal strains, caused by thermal gradients generated by heat of early cement hydration, can be reduced by increasing the maximum size of coarse aggregate, decreasing the slump level and using water reducing admixtures at a given *w/c*. Even the reduction in creep and shrinkage strains, which is particularly important in prestressed concrete structures, can occur by changing the three above parameters in the same way.

Therefore, the development of new and more effective chemical admixtures, which are able to reduce to a greater extent both the amount of mixing water and the cement content would be an useful contribution to reduce creep, shrinkage and thermal strains caused by heat of hydration.

However, there is a limit in reducing the cement content at a given *w/c* which depends on the concrete workability. Mixes that have too little cement paste cannot be pumped and placed without segregation. To overcome this drawback, an exceptional reduction in the cement content (through the use of very high dosages of superplasticizers) could be compensated by a proportional increase in the volume of fly ash. Consequently, the total volume of cement paste including fly ash, which determines the rheological properties of fresh concrete, is not significantly changed. This approach in reducing the cement content has been studied by Malhotra (17). The amount of heat per concrete volume unit, generated during the first week, is proportional to the cement content and does not substantially depend on the amount of fly ash. Therefore, more effective chemical admixtures in reducing the content of cement, replaced by an equivalent volume of fly ash, could be advantageously used in reducing thermal strains generated by heat of hydration in mass foundations or other mass concrete structures, particularly when coarse aggregate with very high maximum size (> 100 mm) are not available.

3. RETARDERS

Admixtures which lengthen setting time and workability time are known as set retarders or retarding admixtures. Retarders are particularly useful for concreting in hot weather where the alternative technique to face up to this problem (ice addition to decrease the concrete temperature) is more expensive and may not be readily available at the work site. Attention should be paid to the overdosage of retarders, unless specifically required, because in such a case the retarding action can be prolonged to the early hardening process (1-3 days) and consequently the demoulding of forms should be delayed.

Traditional retarders are substantially based on the same raw materials devoted to the manufacture of plasticizers with different formulation to enhance the retarding effect (18).

Research efforts on the development of new retarders are relatively few (19-22) and have been devoted to the case of "extended" or "super" retarders. Two special applications of these new retarders can be mentioned to improve construction joints and to re-use returned concrete.

The latter application is related to increasing environmental concerns and restrictions regulating the disposal of returned fresh concrete as well as of truck wash water which are both considered to be hazardous waste according to the classification of many environment protection agencies (1). Therefore disposal of plastic concrete and truck wash water is becoming one of the most important problems for the ready-mixed concrete companies. The technique adopted to solve this problem is substantially based on the use of a stabilizer and an activator, where the stabilizer is a special retarder that suspends the cement hydration and the activator is an accelerator that reactivates the process. Depending on the stabilizer dosage, the returned concrete can be kept in a plastic state for hours or days.

4. ACCELERATORS

Accelerating admixtures are chemicals which can increase the rate of early cement hydration and consequently to reduce the setting time or to increase the early strength development at normal or low temperatures. This enables reduction in the curing and protection periods required to achieve designed strengths in concrete (23).

Calcium chloride has been used as accelerator for a long period at least since the year 1873 (23). It is very cheap and effective as accelerating admixture. However, since the presence of chloride ions in concrete can promote the potential corrosion of the steel reinforcement, an alternative to calcium chloride is one of the most important targets for many researchers in the area of chemical admixtures. Many soluble salts such as thiocyanates, thiosulfates, nitrites, nitrates, aluminates, etc. or organic compounds such as triethanolamine or formates have been tried as ingredients for new admixtures which act as accelerators and do not promote corrosion of steel (24-27). However no new admixture is as cheap and performs as well as calcium chloride as accelerator of cement hydration.

Special accelerating admixtures can be considered chemicals which activate the hydration of slag as hydraulic cement in the absence of portland clinker. Activating admixtures for slags (28-32) have been proposed which are based on caustic alkalis, alkali silicate and alkali non-silicate salts. Although they are very effective in activating slags, these chemicals can cause some problems such as efflorescence effects, increase in alkali-aggregate expansion, etc. and more research work is needed to solve these problems.

5. AIR ENTRAINING AGENTS

Air entraining agents are admixtures which are capable to form air bubbles dispersed throughout the cement matrix that binds the aggregate. A given value in the air volume (4-6%) and a proper spacing factor (100-200 μm) are required to produce an adequate air bubbles system to protect concrete from disruptive stresses caused by ice formation (33). However, Whiting and Stark (34) have listed 23 factors that affect air entrainment and therefore frost resistance of concrete. Variabilities in sand grading, cement composition, fly ash, temperature, etc. make difficult to adjust the proper air volume to the required value depending on the maximum size of coarse aggregate. New air entraining agents have been developed which are claimed to be superior over the usual vinsol resin based products in term of evenly spaced air bubbles or more stable air volume (35).

A very interesting and promising new method to produce frost resistant concrete is based on the use of hallow plastic microspheres with size in the range of 10-50 μm (36-39). The microspheres can be deformed and partly destroyed by disruptive hydraulic pressure caused by ice formation. However, the original voids into the hollow plastic microspheres are still able to provide empty escape spaces for the excess water where freezing occurs. This method appears to be more reliable than that based on the air entrainment, because the dosage of plastic microspheres is much more accurate than the formation of air bubbles.

The main limit in the use of plastic microspheres appears to be the high cost in comparison with that related to air entrainment.

6. ALKALI-AGGREGATE REACTION INHIBITORS

The alkali-aggregate reaction (A.A.R.) inhibitors are chemical admixtures which should be capable of reducing the expansion of concrete caused by A.A.R.. The most known method of mitigating the effect of A.A.R. is to incorporate pozzolans or slag and/or to reduce tha alkali content in the mix. However, a reliable method of

utilizing reactive aggregates has not yet definitely found and the problem is expected to become more important in the future because of the shortage in sound aggregates all over the world.

Therefore, the possibility of using chemical admixtures to reduce the expansion caused by A.A.R. has been taken into consideration in the early '50s, and recently there has been a resurgence of interest in the development of chemicals to inhibit the expansion caused by A.A.R. (1).

The chemicals that have been proposed to inhibit the expansion caused by A.A.R. include mainly salts of lithium (about 1%) and barium (about 2-7%) besides other organic and inorganic compounds. However, these chemicals are either very costly (lithium salts) or inconsistent for their performances and may cause adverse side effects such as strength loss, etc. (40).

Contradictory explanations on the mechanism have been suggested for lithium carbonate as A.A.R. inhibitor: lithium silicates would be produced in form of either soluble silicates on the surface of reactive aggregates without causing swelling (40) or insoluble lithium silicates that are not imbibed by water and therefore reduce swelling (41). More recent investigation (42) do not confirm the acceptable performances of lithium salts in reducing the A.A.R. expansion and would indicate that other chemicals such as sodium silicofluoride or silane are more effective as A.A.R. inhibitors.

Because of the above limited data, that are even contradictory each other, more research is required to find effective, reliable and cheaper chemicals for this type of admixtures in view of the growing interest in utilizing even aggregates which are potentially alkali-reactive.

7. CORROSION INHIBITORS

Corrosion inhibitors are chemical admixtures which should decrease or prevent the reaction of the reinforcement with the environment and in particular with the chloride salts penetrating through the concrete cover and/or the CO_2 of the air.

Calcium nitrite is perhaps the most popular corrosion inhibitor available on the market and has been proposed to inhibit steel corrosion promoted by chloride (40) as well as by carbonation (43). More recently organic products based on emulsion of butyl ester oleate have been proposed as corrosion inhibitors (44).

Berke and coworkers (45) have extensively studied the performances of calcium nitrite and they have found that this product is an effective corrosion inhibitor. On the other hand, Sakai and Sasaki (46) have found that a nitrite-based corrosion inhibitor was effective only in 5-year exposure tests, whereas in 10-year exposure tests the degree of corrosion the reinforcements was higher in the presence of nitrite than when the admixture was not employed. Collepardi et al., have found that nitrite-based admixtures are not effective as corrosion inhibitors in concrete structures with cracked cover (47).

In view of these contradictory results more research efforts should be devoted in the coming years to the development of reliable and effective chemicals as corrosion inhibitors, particularly for reinforced concrete structures exposed to the potential risk of cracking.

8. CONCLUSIONS

In coming years there will be an increasing demand for the development of concrete construction with special performances that will be able to resist the aggressive actions of environments, such as off-shore structures, sewage pipes, underwater concreting ocean sea floor tunnels, structures exposed to chemical and radiactive materials. For the utilization of waste materials and solidifications of hazardous by-products, special concrete mixes will be needed (1, 39). Moreover, special cement mixes will be required for repairs of infrastructural deteriorated concrete works such as dams, highways, bridge decks, etc.

For all these applications superplasticizers alone or in combination with mineral additions, such as fly ash or silica fume, will play a very important role. More effective superplasticizing admixtures with higher capability in reducing *w/c* as well as slump loss will be required to produce durable and high strength concrete.

More reliable air void systems to produce frost resistant concrete are also needed, and plastic hallow microspheres instead of air entraining agents could be used provided that more economical materials will be available.

New chemical admixtures, including alkali-aggregate expansion reducers and corrosion inhibitors, will be required to produce more durable concrete structures, whereas new retarding admixtures for re-use of returned concrete will be required to face up to the environmental concerns and restrictions for the disposal of returned plastic concrete and truck wash water.

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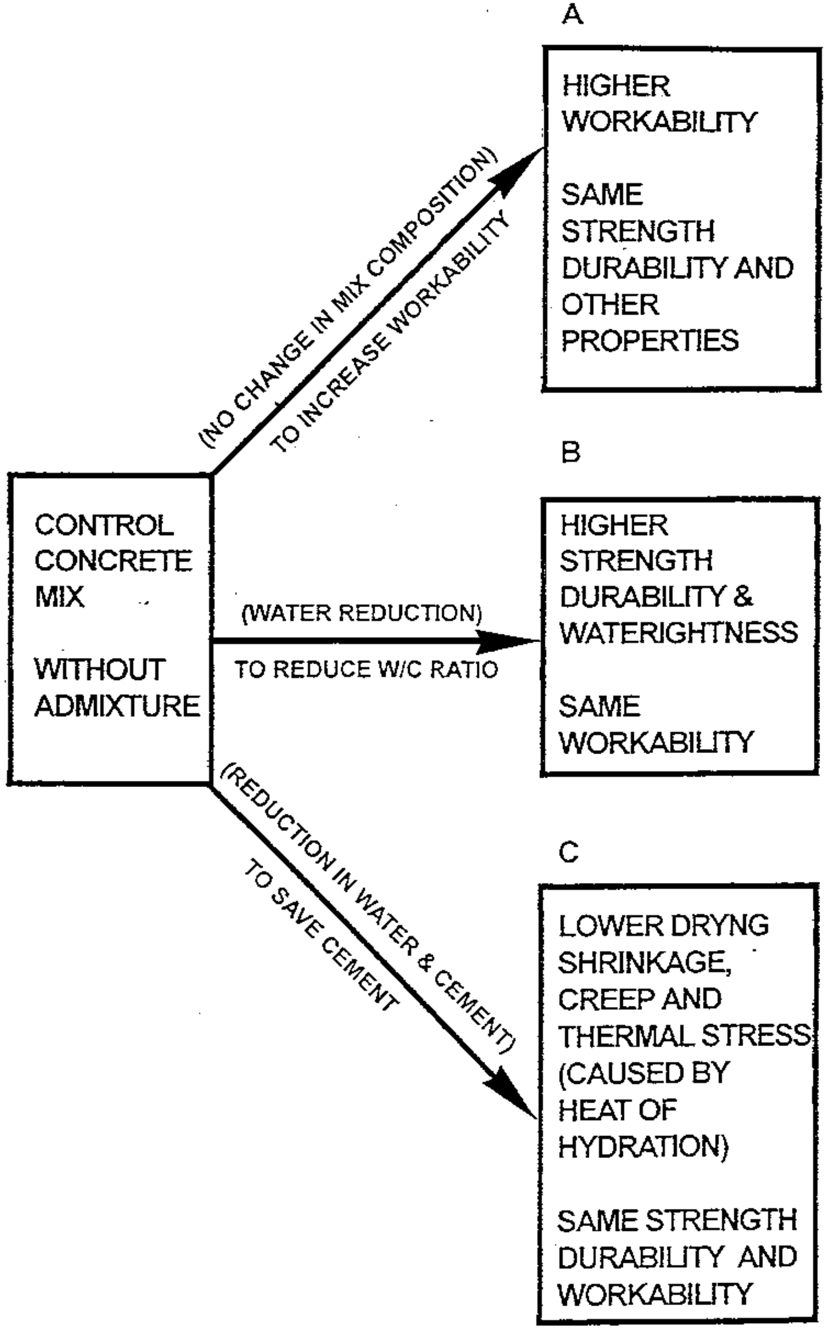

Fig. 1 - Schematic diagram illustrating the effect of plasticizers and superplasticizers on the properties of concretes with these admixtures.

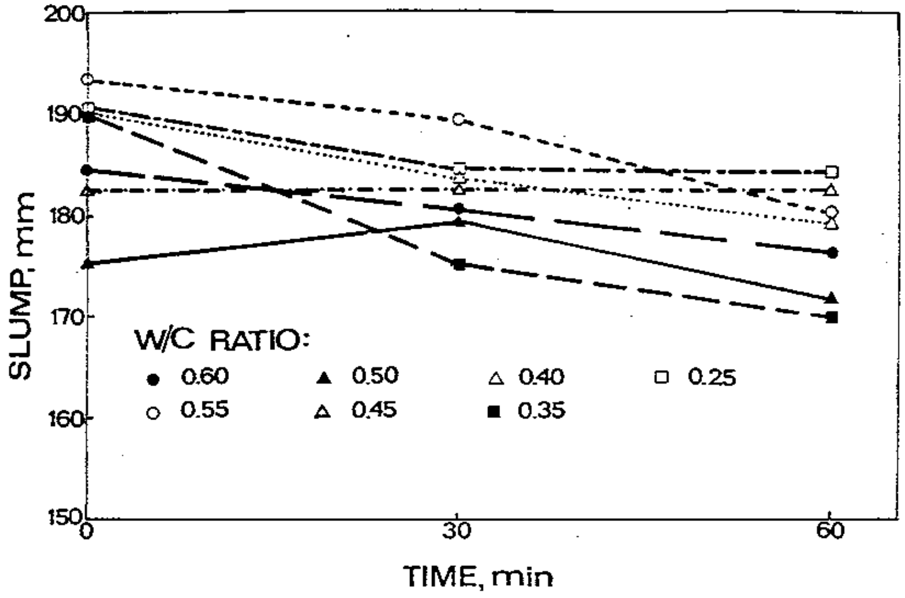

Fig. 2 - Slump-loss curves with a new bicomponent superplasticizer (10).

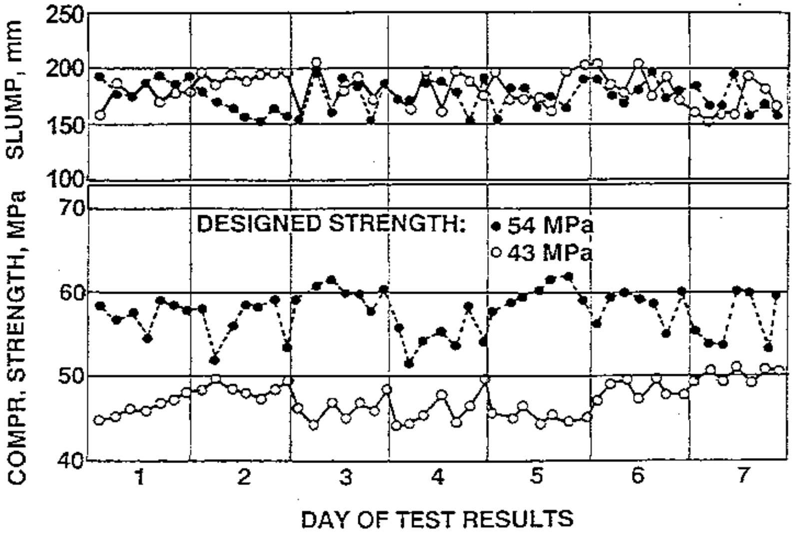

Fig. 3 - Slump and 28-day compressive strength of 49 concrete batches produced in 7 different days (12).

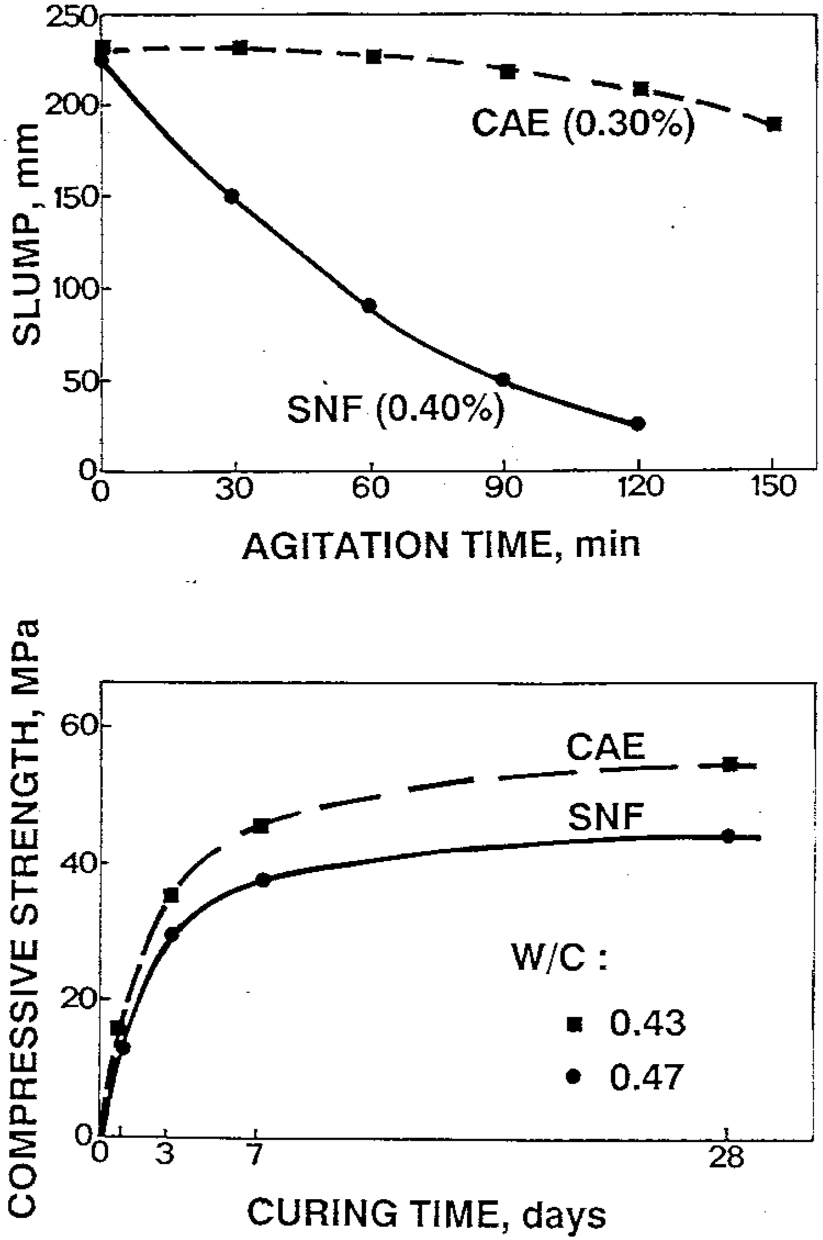

Fig. 4 - Slump-loss (A) and compressive strength (B) at 21°C of superplasticized concretes with OPC and CAE or SNF polymer based admixtures. The figures on the slump loss curves indicate the percentages of the superplasticizer active ingredient by weight of cement (13).