Superplasticizers: A Global Review with Emphasis on Durability and Innovative Concretes

by V.M. Malhotra

Synopsis: This review paper traces the development of superplasticizers in Japan and Germany, describes briefly their mode of action, and discusses the properties of superplasticized fresh and hardened concrete. Data are presented on the use of superplasticizers in Australia, Canada, Japan, Singapore, U.K., U.S.A. and Western Europe. The performance of superplasticized concrete under freezing and thawing conditions both in the laboratory and in the field is discussed, and the use of superplasticizers in the development of innovative concretes is described. The ASTM and Canadian specifications dealing with superplasticizers are discussed, and the paper is concluded with a list of pertinent references.

Keywords: admixtures; concretes; fiber-reinforced concretes; fly ash; freeze-thaw durability; performance; plasticizers; reviews; shotcrete; silica fume; water-reducing agents

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INTRODUCTION

Historically, lignosulphonates have formed the basis of water-reducing admixtures in the U.S.A. and elsewhere, since the early 1940's. However, research in the early 1960's in Japan and Germany led to the development of superplasticizers (high-range water-reducing admixtures). In Japan, Hattori and co-workers (1) pioneered the development of formaldehyde condensates of beta-naphthalene sulfonates with the primary aim of significantly reducing the water demand of concrete admixtures in order to produce high-strength concrete. Water reductions of up to 30 per cent were achieved with the use of one type of superplasticizer. This admixture was introduced into the Japanese market in 1964 and since then, it has gained considerable acceptance in the concrete industry. In Germany, Aignesberger and his colleagues (2) developed the melamine based superplasticizer with the primary aim of producing what is now known as "flowing concrete". The admixture was introduced into the German market in the early 1970's.

The first known use of superplasticizers in North America was in 1975 when melamine-based admixtures were used in the fabrication of large precast concrete units of the Montreal Olympic Stadium which is an outstanding example of segmental concrete construction (3).

The First and Second CANMET/ACI International Conferences on the Development and Use of Superplasticizers in Concrete were held in Ottawa, Canada in 1978 and 1981, respectively. These conferences gave considerable impetus to the use of superplasticizers in Canada, the USA and other countries (4,5).

This paper gives a global review of the use of superplasticizers in concrete. The performance of superplasticized concrete in a freezing and thawing environment, and the role of superplasticizers in the development of innovative concretes is given special emphasis, because other properties of fresh and hardened concrete are adequately discussed in various publications (4,5).

CLASSIFICATION OF SUPERPLASTICIZERS

Superplasticizers may be classified into the following four categories:

1. Sulphonated melamine-formaldehyde condensate
2. Sulphonated naphthalene-formaldehyde condensate
3. Modified lignosulphonates
4. Other superplasticizers such as sulphonic-acid esters, carbohydrate esters, etc.

Significant variations exist in each of the above four categories. The molecular weight of the superplasticizers may vary from less than 100 to 100,000 (6).

MODE OF ACTION

It is generally agreed that the action of superplasticizers is primarily due to their being adsorbed on cement particles and exerting an electrostatic repulsion. This results in the dissociation of the cement agglomerates into primary particles with a significant decrease in the viscosity of the cement/water/superplasticizer system. Superplasticizers may also contribute to the decrease in the surface tension of water and to producing lubricating films at particle surfaces (7). An in-depth study of the rheology, adsorption, hydration and zeta potential characteristics of cement paste and mortars provides a better understanding of the role of superplasticizers in cementitious systems (6).

EFFECTS OF SUPERPLASTICIZERS ON THE PROPERTIES OF FRESH AND HARDENED CONCRETE

Considerable data have been published on the properties of fresh and hardened superplasticized concrete (4,5,8) and a detailed discussion is beyond the scope of this paper. However, some significant properties of fresh and hardened superplasticized concrete are described below.

Properties of Fresh Concrete

There is no undue segregation or bleeding of concrete incorporating superplasticizers when proper concrete mixture proportions and correct dosages of superplasticizers are used. The setting time of superplasticized concrete is sometimes delayed, especially when lignosulphonate-based superplasticizers are used, but this is of no serious consequence in concrete operations.

The entrained-air content of fresh superplasticized concrete may show some decrease with time. It, therefore, may be important that air content of fresh concrete be determined immediately after mixing, and before casting test specimens.

The large increases in slump of the superplasticized concrete are of short duration, and within 30 to 60 minutes the concrete reverts back to its original slump. This problem can generally be overcome by the use of a retarded version of the superplasticizers and the use of repeated dosages of the admixture (9).

Properties of Hardened Concrete

The increase in the mechanical properties, i.e., compressive and flexural strengths and modulus of elasticity, is generally commensurate with reductions in water content when superplasticizers are used as high-range water-reducers (8). Compressive strengths approaching 100 MPa with corresponding increase in flexural strength and modulus of elasticity have been achieved with the use of superplasticizers. The use of silica fume is not essential in superplasticized concrete if the compressive strength requirement is in the order of 80 MPa.

The general consensus appears to be that concrete incorporating superplasticizers has approximately the same shrinkage and creep as the reference concrete, though there are exceptions (8).

WORLDWIDE USE OF SUPERPLASTICIZERS

Since their introduction in the early 1960's in Japan, and in the early 1970's in Germany, the use of superplasticizers has increased dramatically in Japan and several countries in Europe. Superplasticizers are also being used increasingly in developing countries and eastern Europe where indigenous products have been developed. In North America, the acceptance of superplasticizers was slow in the beginning. This was due primarily to conservatism of the construction industry and marketing problems experienced by the Japanese and the European manufacturers. This was further compounded by the fact that initial investigations performed by the Corps of Engineers, U.S.A, indicated poor performance of superplasticized concrete in rapid freezing and thawing tests conducted in accordance with ASTM C 666 Procedure A (10). Lately, both the technical and marketing issues referred to above have been resolved, and the use of superplasticizers is on the increase in North America. Table 1 provides some data on the current usage of superplasticizers by the ready-mixed and precast concrete industry in various countries. The very low usage of superplasticizers in France and the U.K. is worth noting.

DURABILITY OF CONCRETE INCORPORATING SUPERPLASTICIZERS

Soon after superplasticizers had been introduced into North America, questions were raised as to the freezing and thawing durability of concrete incorporating these new admixtures, both in the rapid freezing and thawing tests, and in in-place concrete (10). It is now recognized that although the bubble spacing factor ($\bar{L}$) of superplasticized concrete may exceed the established limit of 0.2 mm, this in no way impairs the durability of the superplasticized concrete (11).

Durability of Superplasticized Concrete in Laboratory Rapid Freezing and Thawing Tests

CANMET has been investigating the durability of air-entrained superplasticized concrete using ASTM test method C 666 Procedure A (rapid freezing in water and thawing in water). These investigations have led to the following conclusions (11).

Non-Air-Entrained Concrete

Non-air-entrained concrete prisms, regardless of the water-to-cement ratio, when tested in accordance with ASTM C 666 Procedure A (freezing in water and thawing in water) show very low durability factors (<31).

Non-air-entrained concrete prisms with water-to-cement ratios of 0.50 to 0.70 show very low durability factors (<12) when tested in accordance with ASTM C 666 Procedure B (freezing in air and thawing in water). However, concrete prisms with a water-to-cement ratio of 0.35 show satisfactory resistance to 300 cycles of freezing and thawing (durability factor >90). Between 300 and 400 cycles the prisms deteriorate markedly. Notwithstanding the strength loss associated with air entrainment, the use of air-entrained concrete is recommended for low water-to-cement ratio concrete for added assurance against damage when concrete is to be subjected to repeated cycles of freezing and thawing.

Air-Entrained Concrete

Regardless of the water-to-cement ratio used, the air-entrained concrete prisms show high durability factors (>90) at the end of 300 cycles of freezing and thawing. This is true for both ASTM C 666 Procedures A and B. However, beyond 300 cycles of freezing and thawing, concrete prisms with a water-to-cement ratio of 0.70 seem to perform poorly in test Procedure A as compared with test Procedure B.

Air-Entrained Superplasticized Concrete

The bubble spacing factors L for air-entrained superplasticized concrete are, in some cases, higher than 0.20 mm. But in spite of the higher values of L, and regardless of the test procedure used, the durability factors for concretes are high (>90) at the end of 300 cycles of freezing and thawing for concrete mixes of Series I*, and at the end of more than 700 cycles of freezing and thawing for concrete mixes of Series II**. These durability factors are compatible with those for non-superplasticized air-entrained concrete.

Durability of In-Place Superplasticized Concrete

Under the U.S.A National Co-operative Highway Research Program (NCHRP) project 10-32, "Durability of In-Place Concrete Containing High-Range Water-Reducing Admixtures", Construction Technology Laboratories, Inc., Skokie, U.S.A, conducted a study of concrete placed with high-range water reducing admixtures (12). Existing concrete bridges and highway pavement and cores from these structures were examined to assess the relationship between durability and air-void characteristics. Although these admixtures have not been in use for very long, the study identified factors that appear to influence the production of high quality durable concrete. The authors of the above study concluded that:

1. "High-range water-reducing (HRWR) admixtures, in themselves, have no significant deleterious effects on the surface durability of portland cement concrete exposed to freeze-thaw environments and deicing agents. Behaviour in these environments is similar to "control" concretes prepared without HRWR admixtures.

2. Those qualities that lead to durable conventional concretes also apply to concretes containing HRWR. Properly air-entrained, low w/c ratio concretes that are workable and easy to finish will, in general, be durable even under severe environmental conditions. Factors that impact negatively upon these qualities, such as additions of water at the job site, difficulty in consolidation, overfinishing, or other poor construction practices, will result in a concrete of questionable durability, with or without the inclusion of HRWR.

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*Series I concrete mixtures incorporated a melamine-based superplasticizer and **Series II concrete mixtures incorporated a naphthalene-based superplasticizer.

3. Those variables having the greatest effects on scaling of concrete surfaces in this study include the w/c ratio of the concrete, the proportional amount of entrained air removed from the surface zone, and the spacing factor, $\bar{L}$, in the concrete as a whole.

4. By themselves, characteristics of the air-void system in concrete, as measured by standard (ASTM C 457) and novel techniques, show little correlation with durability of concrete surfaces. Although spacing factors and specific surfaces in many HRWR concretes fail to meet minimum guidelines established by the American Concrete Institute, other factors, namely the w/c ratio and amount of entrained air removed from the near surface zone, have a greater influence on durability than do air-void characteristics measured in the bulk of the concrete."

SPECIALIZED INNOVATIVE APPLICATIONS OF SUPERPLASTICIZERS IN CONCRETE

The availability of superplasticizers has led to the development of innovative concretes for specialized applications. Some of these concretes are described below.

Superplasticized High-Volume Fly Ash Concrete

Superplasticized high-volume fly ash concrete for structural applications is relatively a new material. In 1985, CANMET commenced work on the development of the above type of concrete and in these investigations an ASTM Class F fly ash was used in proportions of 50 to 60 per cent of the total cementitious material (13). Low unit water content (<115 kg/m^3) and a high degree of workability were obtained by the use of high dosages of superplasticizers. This type of concrete had very low water-to-cementitious materials ratio (<0.35), adequate early-age compressive strength (>9 MPa at one day), very high later-age strength (>60 MPa at one year), very low permeability (<500 coulombs in rapid chloride ion permeability test), and satisfactory resistance to freezing and thawing in ASTM C 666 Procedure A test method. Because of its low cost, very low permeability, and very low heat of hydration, this material offers excellent scope for use in a variety of applications such as thick retaining walls, bridge piers and mass concrete.

Steel or polypropylene fibers can be incorporated in high-volume fly ash concrete to give it added versatility.

Superplasticized High-Strength Silica-Fume Concrete

Superplasticized silica-fume concrete is being used increasingly for repairs of structures where impermeability of concrete is of paramount importance (14). This type of air-entrained concrete incorporates 400 to 500 kg/m^3 of cement, and 8 to 10% silica fume and moderate dosages of superplasticizer to keep the water-to-cementitious materials ratio to about 0.30. These concretes have high compressive strength (>70 MPa at 28 days) and very high resistance to the penetration of chloride ions (<500 coulombs in rapid chloride ion permeability test).

Superplasticized Fibre-Reinforced Concrete

The incorporation of steel or polypropylene fibres in concrete reduces greatly its workability. This has been one of the serious drawbacks of fibre-reinforced concrete. The incorporation of superplasticizers in fibre-reinforced concrete overcomes this problem of reduced slump, and has led to the increasing acceptance of superplasticized fibre-reinforced concrete, especially for the repair and rehabilitation of deteriorated concrete structures. Fig. 1 shows the concrete piles at Saint John's harbour before and after repair using superplasticized steel fibre-reinforced concrete. The mixture proportions of the air-entrained concrete were as follows (15):

Cement CSA Type 50 (ASTM Type V)	415 kg/m^3
Fly Ash ASTM Class F	105 kg/m^3
Natural Sand	880 kg/m^3
Coarse Aggregates (10 mm max.)	665 kg/m^3
Collated Steel Fibres (Length 50 mm) (Diam. 0.5 mm)	74 kg/m^3
Specified 28-day Compressive Strength	41.4 MPa
A.E.A.	800 mL/m^3
Superplasticizer	6 L/m^3
Water/Cementitious	0.40

Superplasticized Heavy-Weight Concrete

Superplasticizers have been successfully used to increase the density of heavy-weight concretes by reducing the amount of water and lowering the water-to-cement ratio*.

Superplasticized Fibre-Reinforced Shotcrete

The mixture proportions for wet-mix superplasticized fibre-reinforced shotcrete are similar to those of the superplasticized fibre-reinforced concrete described above,

*CANMET Unpublished Data

except that the "shotcreting" method of placing concrete is used. The fibres can be either of steel or polypropylene depending on the job requirements. The fibres are added to the shotcrete to improve ductility and energy absorption (toughness and impact resistance). The fibres can also be used to control thermal and drying shrinkage cracking (16). Fig. 2 shows the repairs of a harbour berth base using wet shotcrete. Typical mixture proportions and properties for wet-mix superplasticized shotcrete are as follows (16).

Normal Portland Cement (Type 10)	400 kg/m^3
Silica Fume	56 kg/m^3
10 mm Coarse Aggregate (SSD)	460 kg/m^3
Concrete Sand (SSD)	1100 kg/m^3
Water	180 kg/m^3
Water-Reducing Admixture	2 L/m^3
Superplasticizer	7 L/m^3
30 mm Steel Fibre	60 kg/m^3
Air-Entraining Admixture As required for	
Air Content (in place)	7 ± 1%
Slump	80 ± 20 mm
Minimum 28-Day Compressive Strength	40 MPa

NATIONAL STANDARDS ON SUPERPLASTICIZERS

Several countries including Canada and the U.S.A have issued specifications for the use of superplasticizers in concrete. Canadian Standard CAN3-A266.6-M85 covers the use of superplasticizers for both water-reduced and flowing concrete; ASTM C 494 and C 1017 deal with the use of superplasticizers in water-reduced and flowing concretes, respectively. Both of these specifications have requirements for minimum durability factors; the Canadian specification goes further and even recognizes the fact that with air-entrained superplasticized concretes, the bubble spacing factor ($\bar{L}$) can exceed 0.20 mm, a limit which is ordinarily specified for air-entrained concrete.

Tables 2 and 3 give physical requirements for the use of superplasticizers in concrete according to CAN3-A266.6-M85, ASTM C 494 and C 1017. ASTM C 494 defines high-range water-reducing admixture as an admixture that reduces the quantity of mixing water required to produce concrete of a given consistency by 12% or greater. Because of the availability of more efficient high-range water-reducing admixtures in recent years, ASTM should consider revising the above value to 20% or greater.

OUTSTANDING ISSUES STILL TO BE RESOLVED

When superplasticizers were introduced in North America, immediate concerns were the loss of workability of superplasticized concrete after about 20 minutes, and the potential durability of such concrete under freezing and thawing conditions. During the intervening years, these issues appear to have been resolved. The loss of workability can be overcome by the use of retarded versions of the products, or by the use of repeated dosages.

As mentioned earlier, the durability of superplasticized concrete is no longer a contentious issue. The problems that still need to be resolved include compatibility of superplasticizers with different types of cements, supplementary cementing materials and other admixtures, the role of alkalies and SO_3, and the possible loss of bond between structural steel and superplasticized concrete in structural slabs. Rapid quality control methods to check uniformity of superplasticizers are needed. It is hoped that the research currently being undertaken by various institutes will lead to the resolution of these issues in the near future.

CONCLUDING REMARKS

The development and use of superplasticizers has revolutionized the manner in which concrete is being transported, placed and compacted. High-strength concretes having compressive strength exceeding 70 MPa at 28 days are being routinely made using the new admixtures.

The judicious use of superplasticizers has led to the development of innovative concretes such as high-volume fly ash concrete, superplasticized fibre-reinforced concrete and shotcrete and high-strength silica-fume concrete with very low permeability.

Problems associated with the loss of workability with time, and the freezing and thawing durability of the superplasticized concrete have been primarily resolved. Research is needed to resolve other issues such as compatibility between the superplasticizers and various types of cements and supplementary cementing materials. Rapid methods to control quality of the superplasticizers are needed.

In 1980, the writer had concluded an ACI paper with the following statement (8).

> "There have been very few major developments in concrete technology in recent years. The concept of air entrainment in the 1940's was one - it revolutionized concrete