

The Concept of Superplasticized Concrete

By P. C. HEWLETT

Synopsis: The meaning of the term superplasticised concrete and the concept to which it relates together with a brief outline of its development are described. Comparisons are made with this type of concrete and that regarded as conventional. Distinction is made between high workability/normal water content concrete as opposed to high strength/low water:cement ratio concrete.

The dependence upon mix design, admixture addition and type as well as method of mixing and placing receive attention. The fluid stage and hardened concrete properties are discussed.

Practical applications of the concept are mentioned and coupled with costs.

Keywords: admixtures; concrete construction; concretes; construction costs; high-strength concretes; mixing; mix proportioning; placing; plasticizers; water-cement ratio; water content; water-reducing agents; workability.

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INTRODUCTION

To prevent ambiguity when dealing with the concept of superplasticisers and superplasticised concrete it is important to clearly define the terms used.

Superplasticised concrete is conventional concrete containing a chemical admixture of the superplasticising type. Two main categories of superplasticiser form the basis of most proprietary admixture types. For instance,

Category A type - based upon sulphonated melamine/formaldehyde condensates.

Category B type - based upon sulphonated naphthalene/formaldehyde condensates.

Conventional concrete is mentioned as the starting point since we are, by and large, concerned with concrete made from usual cements, coarse and fine aggregates. Whilst superplasticised concrete mix design requires a particular fines component in the aggregate, even so, the concept is not "special" in the basic concreting materials sense. The uniqueness of superplasticised concrete stems from the properties imparted to the concrete as a result of the addition of one of these new admixtures. The concrete is novel on two counts:

1. If the superplasticiser is used as a concrete workability improver, then the normal slump concrete becomes "flowing concrete". This is concrete having a slump equal to 200mm (8") or more, a compacting factor of

approximately 0.98 and a Flow Table (1) value within the range 510-620mm (20.4-24.8"). In addition to having high workability, flowing concrete should not exhibit excessive bleeding or segregation. Abnormal retardation and air entrainment should also be absent. Flowing concrete is also referred to as self-compacting concrete, Flocrete, collapsed slump concrete and Soupcrete. All the terms relate to the same workability state of the concrete.

2. As with conventional workability or plasticising admixtures, one can take advantage of the enhanced workability state to make reductions in the water content of superplasticised concrete, whilst maintaining conventional workability levels, namely 50-70mm (2-2.8") slump. Concrete in this state is sometimes referred to as "water reduced" or "high strength" concrete.

Whilst the use of superplasticised concrete is relatively new in some countries such as the U.K. it is not a new concept in Germany and Japan. It is really from these countries that its use has grown into a substantial practice, both for normal construction and in the precasting industries.

The usage of placed superplasticised concrete has now reached several million cubic metres and, "in service" case histories extend over a period of some 12-13 years. In this respect the concept of, and admixture materials used in superplasticised concrete are established and not a sudden departure from accepted concreting practice. Dispersing admixtures similar to the present superplasticisers were known as long ago as 1935. However, in 1954 L. S. Wertz (2) noted the improved viscosity properties of cement slurries when containing this type of chemical but did not extend the concept to concrete.

Concept Is Novel But Not Radical

The Concept Of Flowing Concrete

It has long been a desirable engineering objective to be able to make concrete that would to all intents be self-levelling and flow like a Newtonian fluid whilst maintaining w:c ratio levels that did not cause bleed, segregation or strength reductions either during or after placing of the concrete. Selecting aggregate and using high sand and cement contents high workability can be achieved but there is a limit to which mix design can be taken whilst maintaining strength and this limit appears to be a slump

value of about 150-180mm (6-7.2"). Even then strengths in relation to cement contents are low.

Concrete designed to have an initial slump of 75mm (3") and suitable as a pump mix will, by the addition of a superplasticiser at the manufacturers recommended dosage (usually 1-6 litres per cubic metre), have its slump increased to something in excess of 200mm (8").

The degree to which concrete can be rendered fluid by means of a superplasticiser depends upon aggregate type, shape and overall grading. There is usually an upper limit on dosage above which the concrete or specifically the cement grout component, becomes so fluid that segregation may result.

The workability state of flowing concrete is quite distinct from conventional concrete in that whilst it remains cohesive, it will flow readily with gentle vibration and is almost self-levelling.

Let us consider some other aspects associated with the concept of superplasticised concrete and its practical use.

Due to problems of transporting high-slump concrete, it is very likely that the admixture will be added to the concrete just before it is used. In addition to the problem of transportation we have to accommodate the time dependence of the high workability effect. Figure 1 shows how flowing concrete gradually reverts to its original workability some 30-90 minutes after dosing with the superplasticiser. The data shown relate to typical truck mixing conditions for an approximately 5-m³ (6.54 cubic yd) load. It is possible, by re-dosing the concrete, to reinstate the high workability. However, repeated admixture additions are not recommended (3) and it is best to use the concrete as soon as possible after dosing. However delays can be accommodated by stopping the mixer and re-starting just before the concrete is to be placed. Continued mix agitation causes a more rapid reversion in workability.

The concept of superplasticised concrete in the fluid state is visually obvious but the conventional methods of workability measurement are inadequate and do not measure the combination of cohesion and ease of flow. There have been attempts to categorise the workability of superplasticised concretes by tests other than the conventional tests of slump, compacting factor VB and Flow table.

Figures 2 and 3 show the variation in "yield value" and "plastic viscosity" for normal, plasticised and superplasticised (flowing) concrete. The latter is characterized by very low yield and viscosity values. The yield

value is related to the extent to which the concrete will flow, whereas the viscosity values are related to the rate at which this flow will occur. The "two-point" workability test is particularly appropriate for high flow concretes (4). The relationship of Flow table and slump for a particular mix is shown in Figure 4. The inadequacy of the slump test is apparent since it is already at its practical limit although with care it is possible to extend its application to 200-220mm (8-8.8").

Flowing concrete gives rise to rapid collapse slump, but the concrete remains cohesive and non-segregating.

Considerable quantities of air are released from flowing concrete. This effect is due to both the normal air release capability associated with plasticising or water reducing admixtures and the lower "viscosity" of flowing concrete which eases the release of entrapped air. Typical residual air content figures are 1.2-2.7%. The cement content limit below which the concept of fluid concrete becomes less obvious is about 200 kg/m³ (335 lb/yd³) of cement.

The properties of hardened flowing concrete are dealt with in The Working Party Report, Section 6.8 (5). The concept does not appear to adversely affect strength development, load deformation/creep aspects, durability or shrinkage. However, two recent publications (6,8) infer that the long term freeze-thaw durability of high-flow superplasticised concrete is significantly lower than an appropriate control concrete. Tynes (6) attributes this reduction to an increase in the bubble spacing factor. Results by Edmeades and Hewlett (7) for "corresponding" concrete are shown in Figure 5. The presence of a superplasticiser in the paste phase shows the opposite trend and durability was improved.

Figure 6 shows the normality of the strength/w:c ratio relationship between flowing and controlled concrete.

The Concept Appears Sound

The concept has been used for practical benefit for instance,

1. Placing of concrete with reduced vibration in areas of close bunched reinforcement, and in areas of poor access. By using flowing concrete, the need to cut or adapt formwork to obtain vibrator access may be obviated.
2. The capability of placing - very rapidly, easily and without vibration - concrete for bay areas, floor slabs, roof decks and similar.

3. The very rapid pumping of concrete. Placing rates of 40 cubic metres per hour (52 cubic yards per hour) have been readily achieved using a Schwing Pump. Indications are that there are fewer operations or problems in handling superplasticised concrete by pump, than with traditional pumped concrete. Pumping pressures are less and generally the equipment can be better utilized. It has been reported (9) that superplasticised concretes have been pumped to heights of 35 m (115') in Germany. The combination of cohesion and yet easy placing properties are well suited to pumping.
4. Placing of concrete by means of tremie pipe, particularly in underwater locations, where the ability to spread some 5-6 m (16.4-19.6') from the discharge point without assistance, gives a marked advantage over traditional tremie designed concretes.

The Concept Has Wide Application In Conventional Construction

To take full advantage of the concept of flowing concrete and to justify the materials costs (£1.50 per m³ * for the admixture) the job should be planned for. Superficially this cost can be reduced by using less labour since flowing concrete is readily placed. However, this type of comparison is an oversimplification since concrete operatives perform other functions such as cleaning up and handling formwork, etc., and hence fewer people may not represent real savings. An alternative stems from the time saving made available with flowing concrete.

Table 1 (5) shows the time needed when placing concrete in selected situations. The example allows for placing by mobile crane direct from a Ready Mix truck.

Where reinforcement is congested or if formwork has to be modified by having vibrator access holes cut into it to aid the placing of normal slump concrete, then the hours per m³ cost can be increased above those given in Table 1.

It is in this type of time consuming operation that flowing concrete is seen to have a real advantage. It may also be necessary to place large quantities of concrete outside normal working hours, involving overtime rates for labour. Alternatively, situations where a time restriction for placing large pours has been imposed can benefit.

* In January 1979 the exchange rate was about 2.02 Dollars per £ Sterling.

Other factors, such as renting of vibrating equipment, finishing of surface are not significant items compared to placing labour costs.

In Table 2 (10) pumping costs are compared for a situation requiring good concrete flow around obstacles and close-bunched reinforcement. The direct cost saving is marginal but time saving is very significant. Speeding the overall job results in savings on "on costs". However, other related activities such as steel fixing and formwork have to be programmed to suit the higher output rates, hence the need for planning.

The Concept Can Show Savings But Must Be Planned For

Water-Reduced High-Strength Concrete

Superplasticisers are also used to allow a very significant water reduction resulting in high-strength concrete. Much of the development for this use of superplasticised concrete has occurred in Japan (11) where superplasticisers have been used to reduce water content by as much as 20-33%, compared with 15-16% when using normal plasticising admixtures. Their use has been to produce water-reduced high-slump concrete.

Trends relating to European concreting practice have been confirmed in the U.K. For instance, typical water reduction for a 1:2:4 mix containing 300 kg/m³ (502 lb/yd³) cement are given in Table 3 (12). This trend is maintained for high cement content mixes (11). Such water reductions can yield noticeable increases in early strengths for similar workability concretes, as shown in Tables 4 and 5. However it has to be noted that workability loss can be rapid with high cement content concretes negating to some degree the improved workability imparted by the use of the superplasticiser.

In general, the strength increases obtained, even at low levels of admixture addition, are well in excess of those obtained by increasing the cement content and without adverse side effects. It may be expected that by reducing the water content 25-35% increases of 50-70% in the 24-hour strength may be obtained under normal conditions and a normal 7-day strength is achieved at 3 days and 28-day strength at 7 days.

The advantageous strength/time trend shown in Figure 7 is usually maintained as the concrete matures.

This early high-strength property is particularly useful in the production of pre-stressed beams and units

where overnight heat curing is normally carried out to obtain 28-day strengths but at 24 hours.

This trend allows reduction in curing time and/or curing temperature giving overall savings on energy requirements.

Concrete having improved early strength allows rapid de-stressing of wire reinforcement and quick mould stripping for pre-cast items.

Figure 8 shows that the detensioning strength in the region of 30 N/mm^2 (4350 psi) is obtained after 6-7 hours as opposed to 22 hours for the control. These data relate to the production of pre-stressed pre-cast concrete lintels (13).

In the U.K. this use accounts so far for something above 40% of total superplasticiser production.

It is not practicable - for usual concretes - to use superplasticisers to make significant cement cost savings as is the case for normal water-reducing agents and they are not recommended for this purpose.

Water Content Reduction Can Save Time, Energy And Money

Some consideration has been given to using the strength accelerating capability of superplasticisers as alternatives to conventional chemical accelerators such as calcium chloride, calcium formate, sodium aluminate and others. In the U.K. proprietary chloride-free accelerators cost approximately £1-£2.10p* per m^3 of accelerated concrete and on this basis the cost comparison does not appear that unfavourable. However, both alternatives are considerably more expensive than calcium chloride and both appear uncompetitive in this respect. None-the-less there is a considerable lobby against the continuing use of calcium chloride (14,15) particularly in situations where the concrete contains steel reinforcement and looking ahead a little both superplasticisers and other chemical accelerators could become viable alternatives.

The strength/w:c ratio property for water-reduced superplasticised concrete follows the normal trend and there is no adverse deviation from the expected strength that can be attributed to the presence of the superplasticiser (5). Nevertheless long term test data are scant (16-20) but that which has been published show good high-strength retention except at very high-dosage levels ($\times 3$ normal), when there is less increase long term than might be expected. Even so all the ultimate strengths were still

above the controls (Figure 9).

It is intended in Germany at least to continue these long-term tests over a 20-year period with results available at 4, 6, 8, 10 and 15-year intervals (17).

Indirect durability tests have also shown that superplasticised concrete made to a fixed workability has enhanced resistance to freeze/thaw cycling, although, that for high-flow concrete appears in some doubt (6,7,8).

There are few results confirming the absence of any long-term corrosion hazard associated with concrete containing a superplasticising admixture. However, published data (5) imply the risk is an unlikely one.

In The Working Party Report (5) the creep, shrinkage and durability properties of water-reduced concrete are mentioned and indications are that these properties are not adversely affected. The data, however limited, may be considered as implying that there is no long term detrimental effect from the inclusion of a superplasticising admixture, as far as gain in strength is concerned.

The Concept Appears Reliable In The Long Term

In summary, the relatively high admixture cost could be more than offset by,

1. In the case of flowing concrete:
 - (a) Increased ease in the rate of placing concrete particularly in difficult situations.
 - (b) Reduced need to vibrate.
 - (c) Perhaps a reduction in manpower.
 - (d) Shortening of programme time.
2. In the case of high-strength, water-reduced concrete:
 - (a) Increased rate of unit construction.
 - (b) Reduced time for high-temperature steam curing.
 - (c) Improved strength properties of pre-cast items, reducing breakage and wastage.

This paper outlines two new concepts offering to the construction industry certain real, practical and materials advantages that may be gained by the controlled and proper use of superplasticised concrete.

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TABLE 1

Typical Concrete Placing Times For Different Situations

<u>Item Being Made</u>	<u>Hours/m³</u>	
	<u>0.4m³ Skip</u>	<u>0.6m³ Skip</u>
Beams	1.40	1.50
Columns	2.00	1.80
Walls (150-200mm)	0.08	0.07
Suspended Slabs	0.07	-

Solid Slabs (Placed direct from truck to slab) 0.45

TABLE 2

Cost* Comparison For Normal And High Flow Concrete Placed By Pump

	<u>Normal Concrete</u>	<u>Superplasticised Concrete</u>
Pump (at £12/hr)	3 hrs = £36	1 hr = £12
Labour (at £2/hr)	6 men x 3 hrs = £36	3 men x 1 hr = £6
Admixture at £1.20/m ³	Nil	40m ³ = £48
Total	£72	£66
Costs/m ³	£1.80	£1.65

* In January 1979 the exchange rate was about 2.02 Dollars per £ Sterling.

TABLE 3

Water Reduction Using Category B Superplasticiser

Admixture dosage	w/c ratio	Water reduction (%)	Slump (mm)*
0	0.6	0	100
Normal	0.57	5	100
Twice normal	0.52	15	100
Thrice normal	0.48	20	100
0	0.55	0	50
Normal	0.48	13	55
Twice normal	0.44	20	50
Thrice normal	0.39	28	45

* 1mm = 0.04"

TABLE 4

Early Strength Of Water Reduced Concrete Containing
Superplasticising Admixture

Admixture dosage	w/c ratio	Flowtable spread (cm)	Cube strength (N/mm ²)*		Change in strength (% over control)	
			1 day	7 days	1 day	7 days
0	0.42	41.5	18.0	54.9	-	-
Normal	0.36	42.0	38.0	62.5	+111	+14
Double	0.33	51.0	49.6	76.3	+176	+39
Quadruple	0.32	43.0	49.1	75.8	+173	+38

TABLE 5

Strength/Admixture Dosage Relationship For High Cement
Content Concretes Containing Category A Admixture

Cement content	Admixture dosage	Cube strength at 1 day (N/mm ²)
500	0	32.6
	Double	59.7
	Quadruple	64.4
600	0	32.7
	Double	65.1
	Quadruple	62.7
700	0	39.8
	Double	61.8
	Quadruple	50.1

* 1N/mm² = 145 psi.

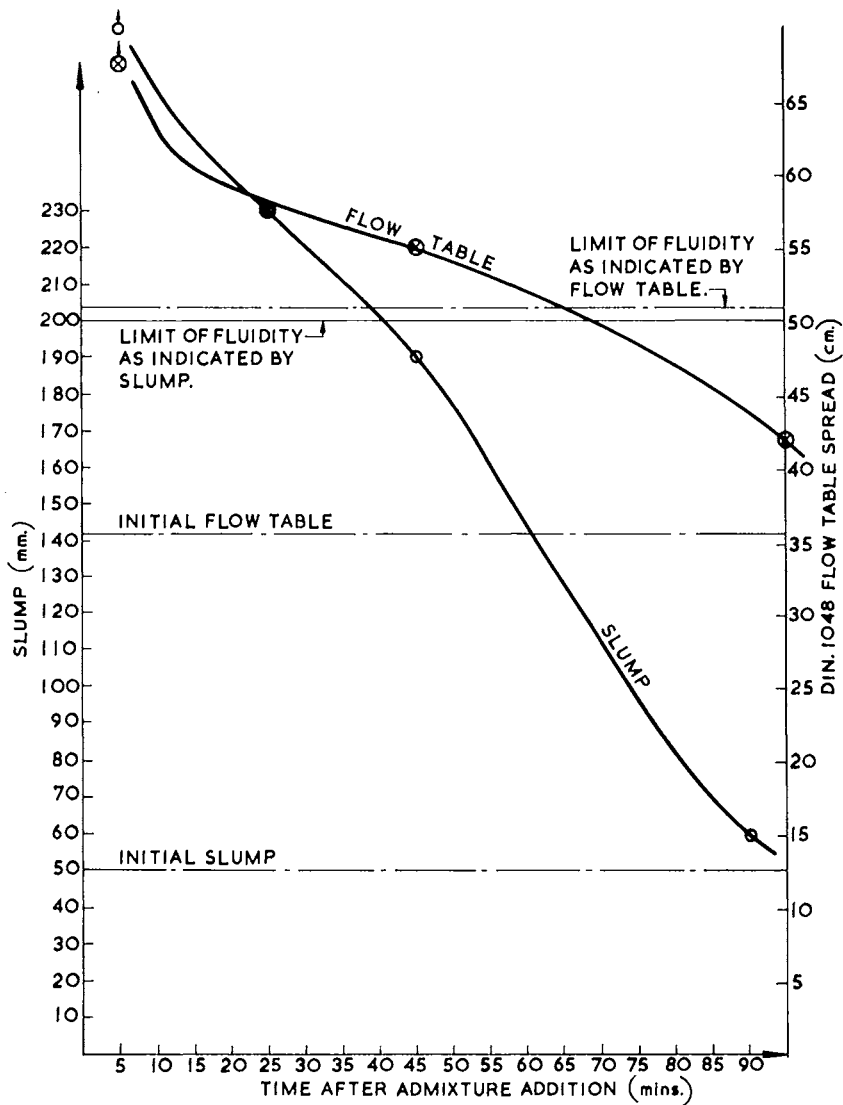


Fig. 1--Time dependence of workability--Category B admixture

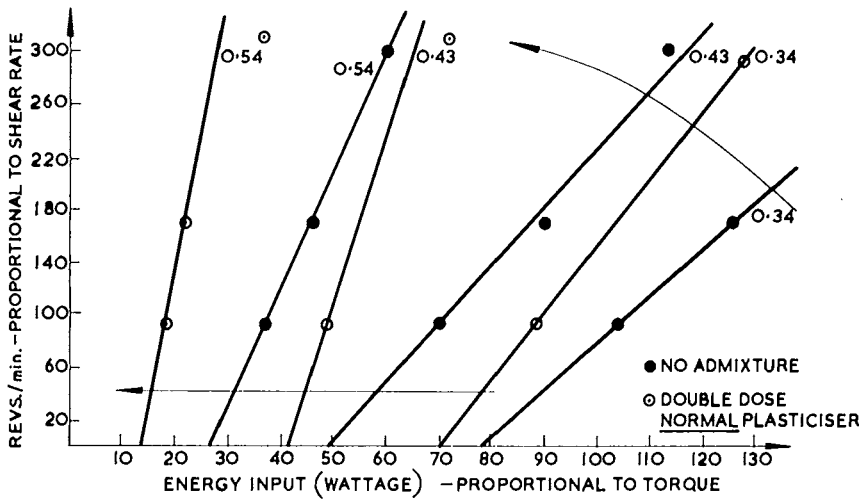


Fig. 2--Rheology of concrete containing normal plasticizer

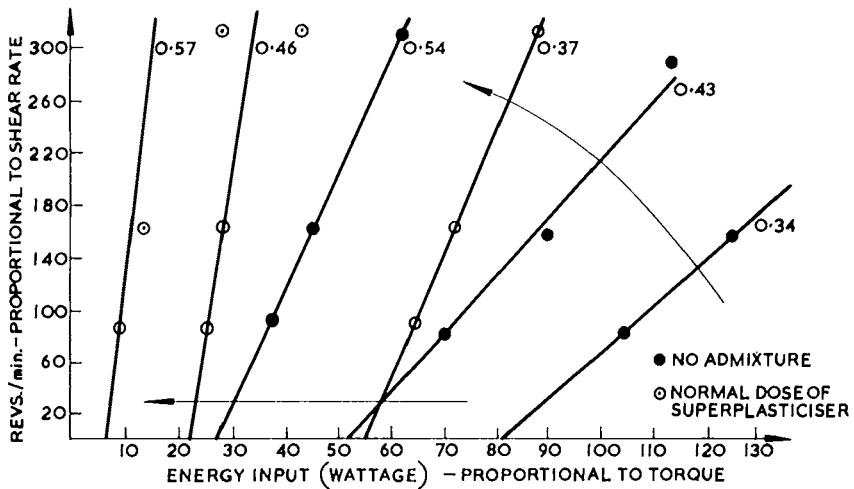


Fig. 3--Rheology of concrete containing superplasticizer--Category B

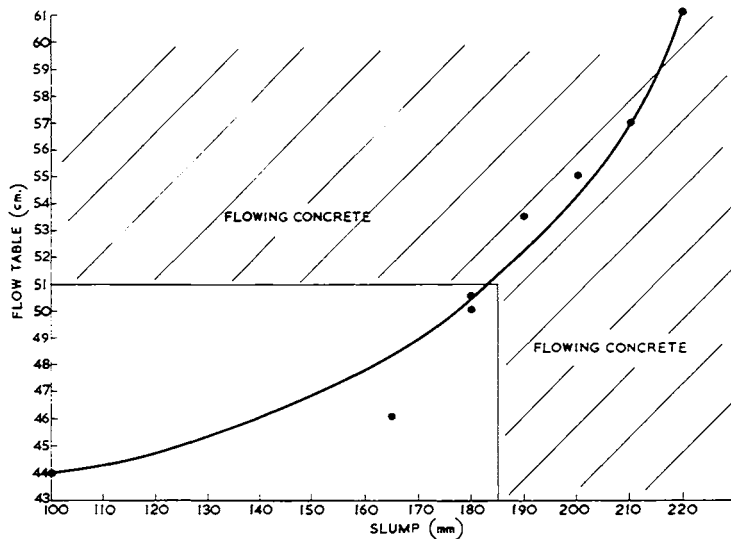


Fig. 4--Flow table versus slump for flowing concrete containing Category B superplasticizer

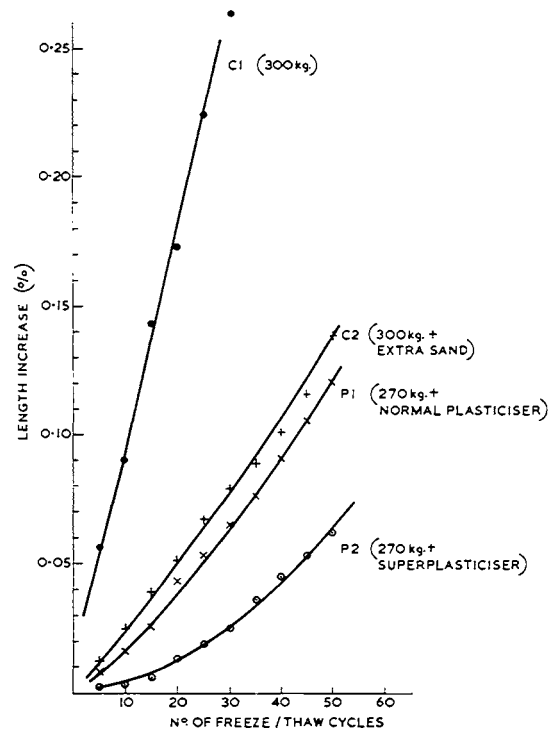


Fig. 5--Freeze-thaw response of "corresponding" concretes containing normal and superplasticizing admixtures

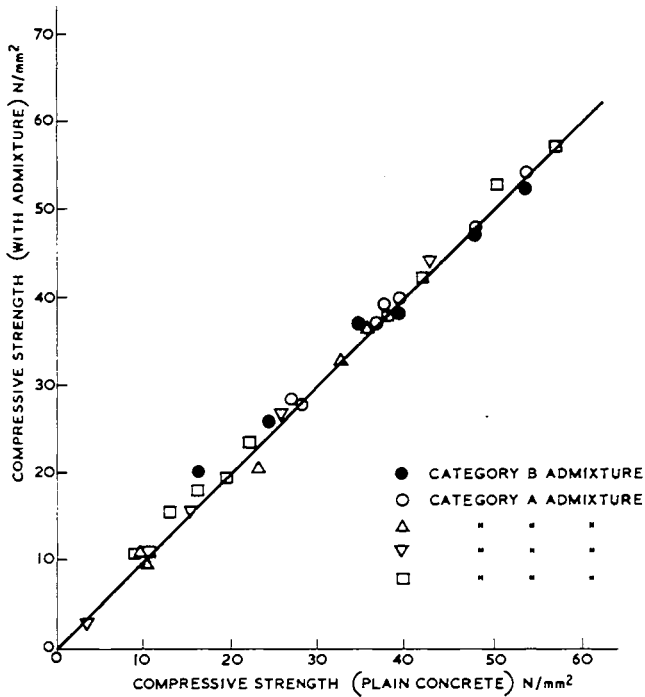


Fig. 6--The relationship between 28-day strength of plain concrete and concrete containing superplasticizers

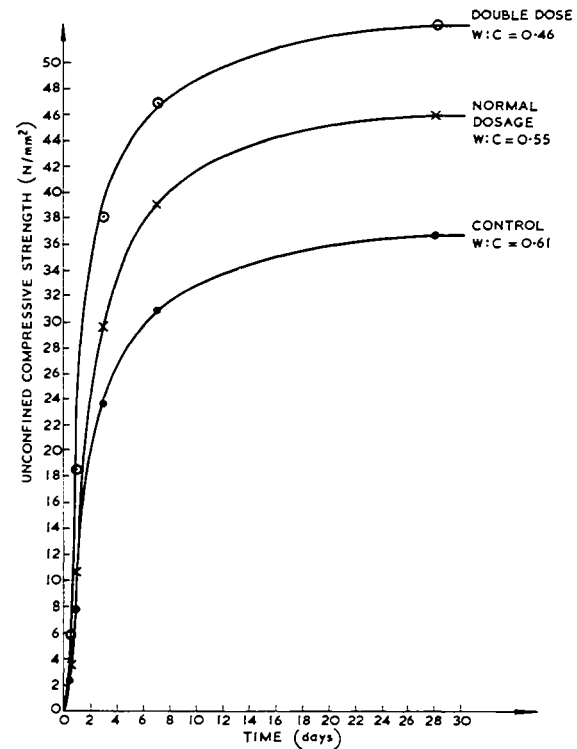
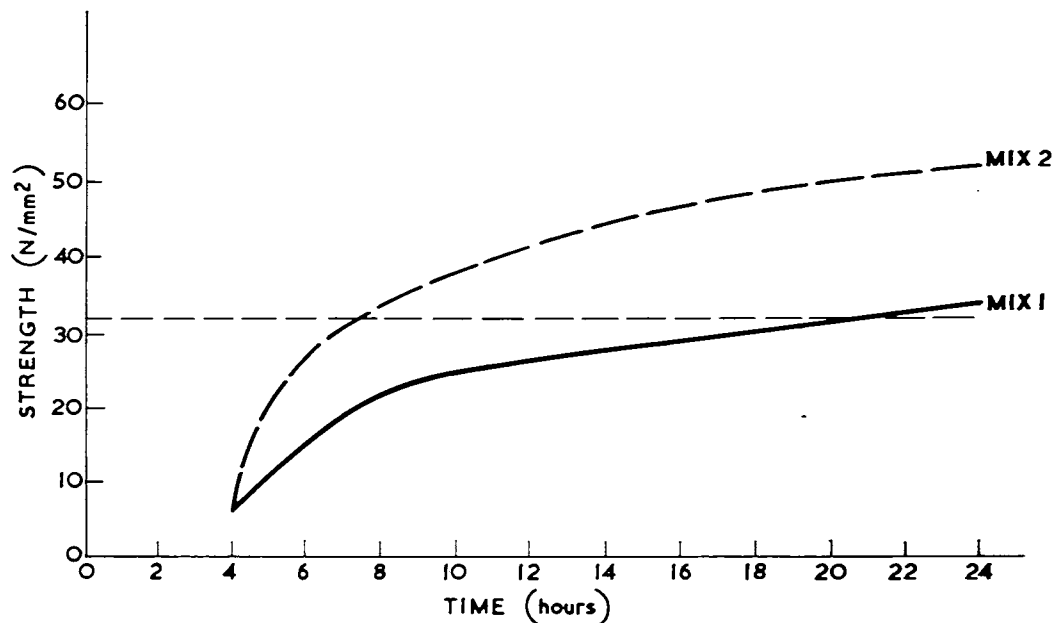


Fig. 7--Strength versus time.
Water-reduced concrete containing
Category A type admixture



MIX DESIGN: AGGREGATE 20mm-10mm ROUNDED GRAVEL, SAND ZONE 3, A/C RATIO 4:1, PERCENTAGE FINES 29, W:C RATIO 0.40 (MIX 1) AND 0.32 (MIX 2) SLUMP 50mm. 28 day STRENGTHS: CONTROL 42 N/mm², MODIFIED MIX 59 N/mm². ADMIXTURE TYPE - CATEGORY B.

Fig. 8--Strength increase of cubes steam-cured under normal conditions showing that the destressing strength (30 N/mm²) is obtained after 6/7 hr compared to 22 hr for the control mix

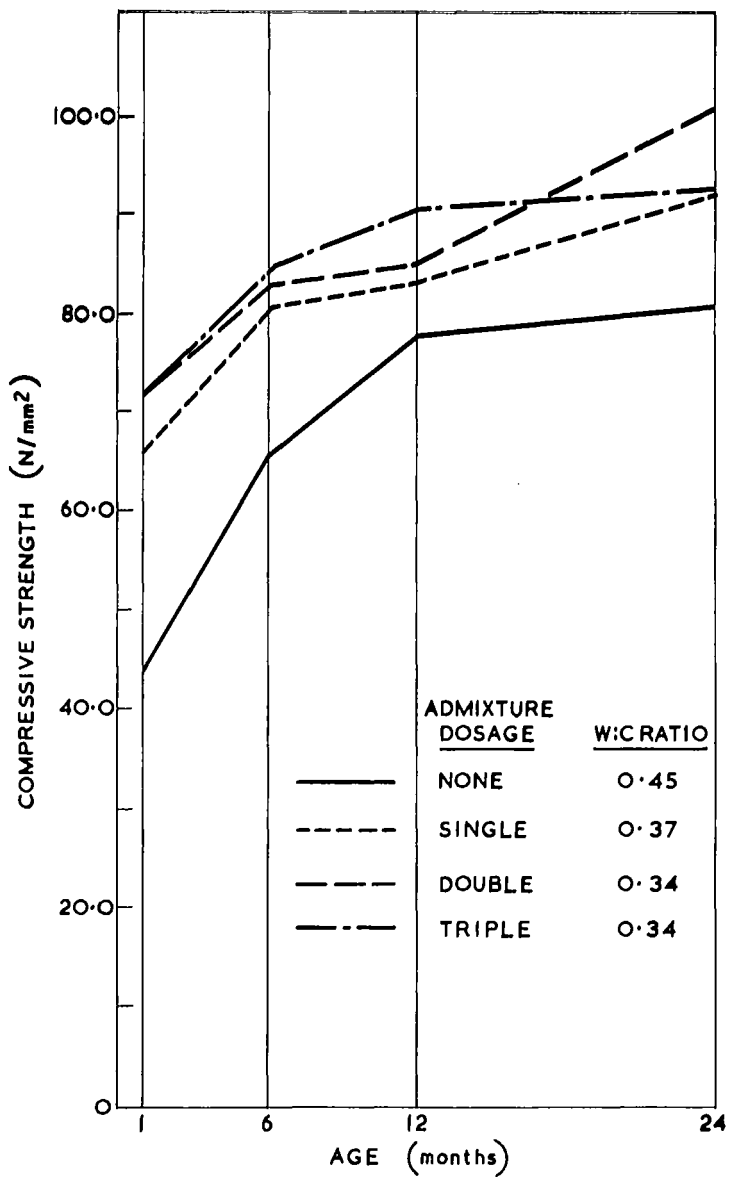


Fig. 9--Long-term strength tests using Category A superplasti-
cizer

Experiences in the Use of Superplasticizers in Germany

By A. MEYER

Abstract: Admixtures that fluidify concrete have been used in Germany for many years to improve the workability of concrete and to reduce its water content.

However, in the 1960's more effective fluidifiers were introduced in Germany and are known as superplasticizers. The real breakthrough in the application of these new types of admixtures came during the early 1970's.

Superplasticizers are natural or artificial polymers, which may be grouped by their chemical composition in several categories. Superplasticizers are used: a) to regulate concrete consistency, b) to produce flowing concrete, c) to manufacture high-quality concrete having low water-cement ratio.

Experiences in the above three areas of application are discussed. Practical hints for the selection of raw materials, dosage of admixture, and performance tests are given. The German guidelines for the Use of Superplasticizers in Concrete are briefly discussed.

Keywords: admixtures; compressive strength; concrete construction; concretes; fresh concretes; plasticizers; plastics, polymers and resins; specifications; water-cement ratio; water content; water-reducing agents; workability.

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Introduction and Historical Background

Hardened concrete having good properties requires the least possible water content consistent with sufficient workability. With decreasing water content, the workability of fresh concrete is reduced and the effort for full compaction increases. For this reason, concrete that has been produced up to now, is compacted by vibration.

Plasticizing admixtures that have mainly a physical influence have been used for many years to reduce water content and improve the workability of concrete. Their effectiveness, however, is limited, because at high dosage levels adverse side effects occur in most cases. Only recently has it become feasible, with the use of new or modified chemicals, to improve the workability without substantially altering other properties of fresh and hardened concrete.

Additives of considerably higher efficiency than those usually available within the range of normal plasticizers, are known in Germany under the terms of "Superverflüssiger" or "Fließmittel"¹, and in the English-speaking world as "Superplasticizers" or "Fluidifiers". These superplasticizers were produced and tested in Germany and in Japan for the first time in the mid-Sixties. Since 1964, concrete with superplasticizers has been used in construction in Germany. The use of superplasticizers for concrete increased rapidly in the Seventies; this, in turn, brought about considerable progress² in certain fields of concrete technology. Kern und Knoch² estimate the volume of flowing concrete used in Germany alone in the mid-Seventies on site at some 2 million cubic metres annually. It should be noted that this amount does not include the volume of concrete with superplasticizers used in precast concrete plants.

Types of Superplasticizers and Requirements

The superplasticizers currently in use may be subdivided into four categories:

- A = sulfonated melamine-formaldehyde condensates
- B = sulfonated naphthalene-formaldehyde condensates
- C = modified ligninsulfonates
- D = other superplasticizers such as sulfonic acid esters or other carbohydrate esters.

Superplasticizers exert their action by:

- a) decreasing the surface tension of water
- b) equidirectional charging of cement particles
- c) producing a lubricating film at particle surfaces (slip action)

Superplasticizers of category A act mainly by forming a lubricating film at the particle surfaces. Superplasticizers of category C decrease the surface tension of the water. Superplasticizers in category B and D only decrease the surface tension of water to a minor degree, but, in addition, they charge the surface cement particles equidirectionally to form a lubricating film at the particle surfaces.

The plasticizing action of superplasticizers must be considerably stronger than that of normal plasticizers, and should last as long as possible. Superplasticizers must be devoid of risks of undesirable reactions with any component of the concrete or of interfering with the corrosion protection of the reinforcement in the concrete. Superplasticizers should not significantly affect the setting and hardening of the concrete, as well as to its pumpability. Unintentional adverse side effects, such as excessive air entrainment, should not occur even at high dosages. Modifications in the properties of the cement, the aggregates, or both, should not influence to any marked degree the efficiency of the superplasticizer.

Superplasticizers in liquid form are preferred to products in powder form, because dispensing is easier and can be made more accurately. It is not recommended to use superplasticizers in doses less than 0.8 % of the cement mass, in order to guarantee prompt and uniform distribution within the mixture.

Liquid superplasticizers should remain stable in storage even at low, ambient temperatures. Superplasticizers should be compatible in use with other additives, such as air-entraining agents or setting retarders. These requirements are more or less fulfilled by the superplasticizers currently available on the market.

Areas of Application

Superplasticizers are being used in Germany for three principal purposes:

- a) control of the consistency of fresh concrete without modifying the properties of the hardened concrete;
- b) production of flowing concrete from stiff concrete
- c) production of high quality concrete at a low water-cement ratio

Figure 1 is a schematic presentation of the interrelationship between the degree of workability measured by the DIN 1048 flow table spread, and the water content of concrete with a Portland Cement content of 300 kg per cubic metre without superplasticizer, and of the same concrete with 1.5 % of a category A superplasticizer.

Figure 2 shows the interrelationship between flow table spread and slump. Workability is improved considerably by adding superplasticizer. Stiff concrete, with low slump, is transformed into a flowing concrete. Both have the same properties in the hardened concrete state.

The first and the only use of superplasticizers in the earlier days was just to modify the consistency and to produce flowing concrete. At a later time, the use of superplasticizers was extended to reduce the water content of concrete without changing its consistency. This will yield a high quality concrete at low water-cement ratio. Of course, it is possible to combine the two methods, improving workability and reducing the water content of the concrete at the same time.

Correcting Consistency

Consistency is a criterion for the workability of fresh concrete. Shortly after mixing, the consistency may change unexpectedly by early hydration of the cement or by loss of water. This latter phenomenon may be brought about by evaporation, by adsorption of water by the forms, or by the use of porous aggregates. Changes in consistency after mixing, in such cases as when fresh concrete has been transported or stored for an extended time, should also be considered. The change of workability may complicate transporting, placing, and good compaction. This can lead to a more or less serious loss of concrete quality. Experience has shown that - especially in case of ready-mixed concrete - consistency will need to be frequently corrected up until it is placed. This is done, in most cases, by adding water to the mixture, although it is a well-known fact that this will bring about a marked loss of quality unless the cement content is also increased in proportion to the water-cement ratio.

It is better and easier to add a superplasticizer to correct the workability.

Figure 3 shows the relation between flow table spread and dosage of a category A superplasticizer.

Subsequent fluidification of the fresh concrete by adding a superplasticizer will not significantly change the water-cement ratio and, as a consequence, will not change the properties of hardened concrete. The result will be a concrete of uniform quality. Most superplasticizers may be mixed into the fresh concrete like water. Selection of mixing time to obtain uniform distribution is normally made by visual inspection. Repeated dosages of most superplasticizers will not cause significant changes in the properties of the concrete. Control of workability by adding a superplasticizer is easy and safe to carry out, and the uniformity of the concrete is also improved.

Flowing Concrete

Definition: Flowing concrete is a fresh concrete displaying good flow properties and, at the same time, satisfactory cohesive properties. Concrete of this nature is obtained from initial stiff, low-slump concrete by subsequent addition of a superplasticizer. The cement and water volumes of the initial concrete remain practically unchanged in the flowing concrete, so that the favourable properties of the initial stiff concrete will remain un-

impaired. Improved workability of the flowing concrete will simplify its placing and reduce the compacting energy. Under equal conditions, flowing concrete will yield a more uniform product than stiff and low-slump concrete.

Application: Flowing concrete is being used on the site particularly for the construction of large surface area warehouse floors and ceilings, as well as for subfloor and foundation slabs.

The use of concrete pumps for these construction operations will result in high placing efficiency at a minimum of labor cost.

The rate for compacting and screeding large concrete surfaces with flowing concrete may be reduced to about 0.15 hours per square metre. For deep-lying foundation slabs, a rate of 0.2 hours per cubic metre of concrete may be obtained. This requires site equipment geared to the handling of flowing concrete, and carefully detailed planning of the supply of flowing concrete to the site.

Where concrete work has to be carried out on slender, reinforced structural elements with a high compressive strength, the use of flowing concrete may prevent the occurrence of defective areas and cavities, thus avoiding a source of potential future damage. Thus a fully compacted, uniform structure of the concrete is guaranteed.

By the use of flowing concrete in precast concrete plants, heavy compacting equipment may be replaced by lighter units, which in turn will result in a decrease of stress on the formwork. The lower amount of compacting energy required with flowing concrete will also bring about a considerable decrease of the noise level during operations. In addition, the exposed surfaces of the prefabricated elements will have a surface with reduced porosity.

Adding the Superplasticizer

The initial concrete without superplasticizer must display good cohesiveness but should not be too stiff. Flow table spread should be between 34 and 44 cm. Very low and very high cement contents are less suitable for the production of flowing concrete. Cement contents from 300 to 350 kg per cubic metre with a maximum aggregate particle size of 32 mm have proven to be most satisfactory. The superplasticizer is added to the fresh concrete immediately prior to its discharge.

In order to obtain a prompt and homogeneous distribution of the additive, the amount should not be too small. An extra mixing time of 1 to 5 minutes, according to the efficiency of the mixer, will be required to distribute the superplasticizer within the mixture. Most superplasticizers may be used in repeated dosages in the event of stiffening of the concrete.

Properties

The plasticizing effect of the additive decreases with time after being mixed; see Figure 4. As the decrease depends on a variety of factors, this behavior should be investigated for each individual case of application.

As a rule, the hardened concrete properties for flowing concrete - including strength, impermeability to water, chemical resistance against frost and deicing salts, creep and shrinkage - will be equal to those of the initial concrete. Where superplasticizers with retarding side effects are used, a certain delay of the hardening development in the early state must be taken into account. As a rule, size and distribution of the air voids in the initial concrete will not be altered by adding superplasticizer. It is, however, recommended to investigate the interrelationship between air-entraining agents and superplasticizers where those two agents are to be used together.

High-Quality Concrete

Definition: High-quality concrete is characterized by a high degree of strength and density, and is produced from a fully compacted concrete mixture having low water-cement ratio. The low water-cement ratio will result generally in a stiff consistency; this will require intensive compaction by vibration.

By adding superplasticizer, it is possible to improve the compactability of concrete. Moreover, this method may help to decrease the water-cement ratio further which, in turn, will bring about increased improvement of concrete quality.

Applications: The requirements established for high-quality concrete may be fulfilled more easily when using superplasticizers. High-quality concrete with superplasticizer may be produced on the site as well as in precast concrete plants. The percentage of high-quality concrete with respect to the overall concrete production has increased steadily in the last years, and is expected to increase further in the near future. Where superplasticizers are being adopted, high-quality concrete may even be obtained by using cements and aggregates with lower quality.

Concrete with superplasticizer can be placed in heavily reinforced sections without or with only light vibration. Its high initial strength allows short stripping times in the production of prefabricated concrete elements.

High-quality concrete is being used increasingly for repair to, or construction of, areas to be exposed to traffic that are required to be ready for use within 1 to 2 days; e.g., repair of city roads or for runways of airports. The placing of this type of concrete is easily workable and less susceptible to a lower degree of care in placing.

Properties: Figure 5 shows the possibilities of water reduction by adding a category A superplasticizer. A remarkable decrease of the water-cement ratio will be obtained without any loss of workability. This again will result in an increase, especially of the early strength properties. At the age of 24 hours; e.g., by adding a superplasticizer, the compressive strength may be almost doubled, as shown in Figure 6. Physically active superplasticizers have proved to be more efficient in this respect than chemically active accelerating agents.

Recommendations for Practical Use

The proper manufacturing of concrete with superplasticizers requires special skills and adequate experience. The personnel assigned to this type of work should be extensively instructed on the peculiarities to be considered in application of superplasticizers, before using them.

Before starting any application, it is necessary to test the initial concrete as well as the concrete with superplasticizer. The test conditions for both mixtures should be as similar as possible to the actual requirements. Special consideration should be given to the fact that the plasticizing effect immediately after finishing the mixing

may be influenced not only by the type of superplasticizer used or by its dosage, but also by the properties of the cement, the grading of the aggregate, the mixture proportions, the fresh concrete temperature, and the time during the mixing process at which the superplasticizer is added. Moreover, the effectiveness of any superplasticizer will decrease with time. In order to study side-effects of the superplasticizer and to evaluate the influence of dosage variations, it appears appropriate, in addition to making tests with normal dosage of superplasticizer, to conduct parallel tests using the double quantity as well as half the quantity of additive.

The three most important factors influencing the action of superplasticizers will be treated by way of examples in Figures 7, 8 and 9.

In Figure 7, the grading limits of aggregates are shown which have proved to be most compatible with superplasticizers. A smooth particle size distribution is recommended. Natural sand and gravel are more appropriate than crushed aggregates.

The content of cement and sand particles between 0.0 and 0.25 mm should not be too low to obtain good cohesive properties, and not too high to guarantee good flow quality, see Figure 8. It has been found suitable for the contents of cement and sand particles in the range 0.0 and 0.25 mm to be 400 kg/m³ for concrete with maximum aggregate sizes of 32 mm, and 450 kg/m³ for concrete with maximum aggregate sizes of 16 mm.

Specifications

During introduction of superplasticizers into concrete practice, it was not always easy to make clear that consistency is not the only criterion to measure concrete quality, and that the drawbacks of conventional high-slump concrete do not apply to flowing concrete with superplasticizer. Otherwise, application of superplasticizers did not present real problems. Two recommendations have been developed to assist the correct use of superplasticizers:

Recommendation for Manufacturing of Flowing Concrete,
May 1974 ³

This recommendation was worked out by a committee of "Deutscher Ausschuß für Stahlbeton". It contains requirements for superplasticizers and for the composition and properties of the initial and the flowing concrete.

The term "Fließmittel" (fluidifier) is restricted to plastifying agents which are capable of extending the flow table spread of an initial concrete at 38 to 42 cm by at least 12 cm. The recommendation further gives guidelines for mix design and the placing of flowing concrete. It lays down the methods of measuring the flow table spread of the initial concrete, as well as of the flowing concrete immediately after adding the superplasticizer, then 30 minutes later, and - for retarding superplasticizers - at later points of time if required. Cohesive properties and uniformity of the initial, as well as of the flowing concrete, should be appraised by visual inspection.

Specification for High-Early-Strength Concrete Pavings
with Superplasticizer

The specification worked out by "Forschungsgesellschaft für das Straßenwesen" will be issued soon. It is intended for regulation of the special features of this type of paving. The term "high-early-strength concrete with superplasticizer" includes high-early-strength flowing concrete at a flow table spread of 51 to 60 cm, and fresh concrete with superplasticizer at a flow table spread of 45 to 50 cm. High-early-strength concrete with superplasticizers is suitable for all types of pavings. Its use is particularly appropriate in cases where the allowable time for disrupting traffic is very short, or where conventional equipment for placing concrete cannot be used due to restrictions of space. Guidelines are given for mix design and placing of high-early-strength concrete with superplasticizer. Depending on the traffic load, minimum compressive strengths of 210 to 280 kg/cm² after 2 days, and 300 to 400 kg/cm² after 28 days are specified. Frequently, this high-quality concrete makes it possible to open the pavement for traffic as soon as 1 to 2 days after concreting.

Other chapters of this specification concern joint cutting, curing and testing.

Concluding Remarks

Superplasticizers have been used for the past ten years in Germany in ever increasing amounts. Concrete with superplasticizer has proved to be technically and economically advantageous in several fields of civil engineering and road construction, as well as in the production of ready-mixed concrete and prefabricated concrete elements. There are still more possibilities to improve concrete placing, concrete quality, as well as to save labor costs, by the use of superplasticizers.

Any further extension of the application of superplasticizers will depend, to a substantial degree, on how far the costs of superplasticizers will be decreased in the future.

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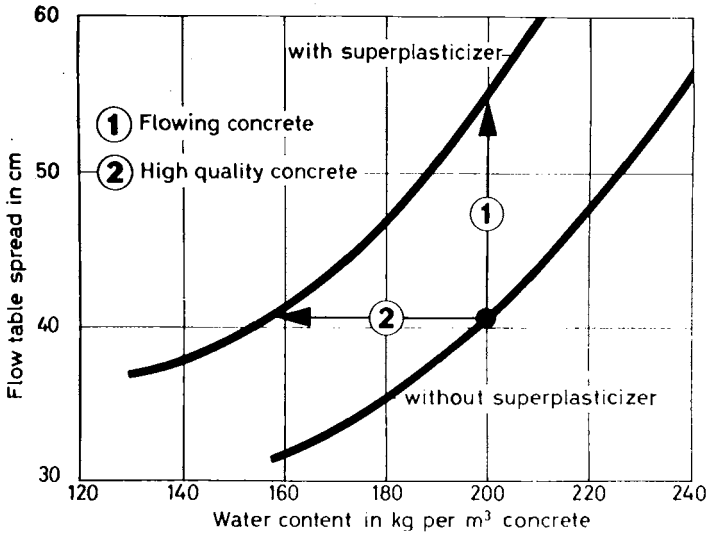


Fig. 1--Relation between flowtable spread and water content of concrete with and without superplasticizer

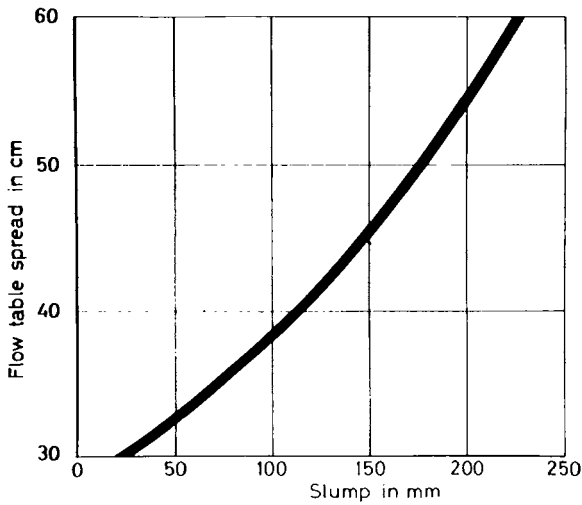


Fig. 2--Relation between flowtable spread and slump

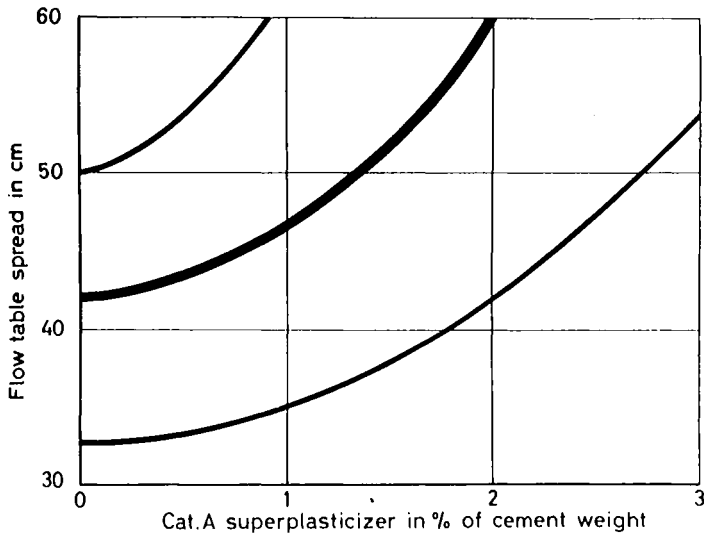


Fig. 3--Relation between flowtable spread and dosage of Category A superplasticizer

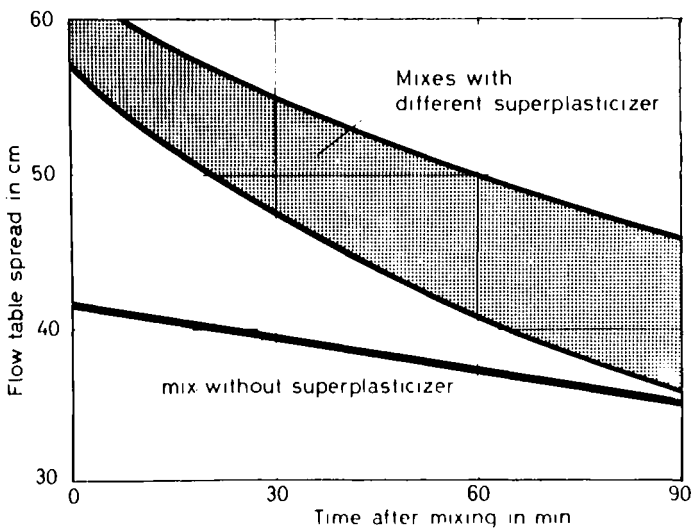


Fig. 4--Time dependent workability for concrete containing superplasticizer

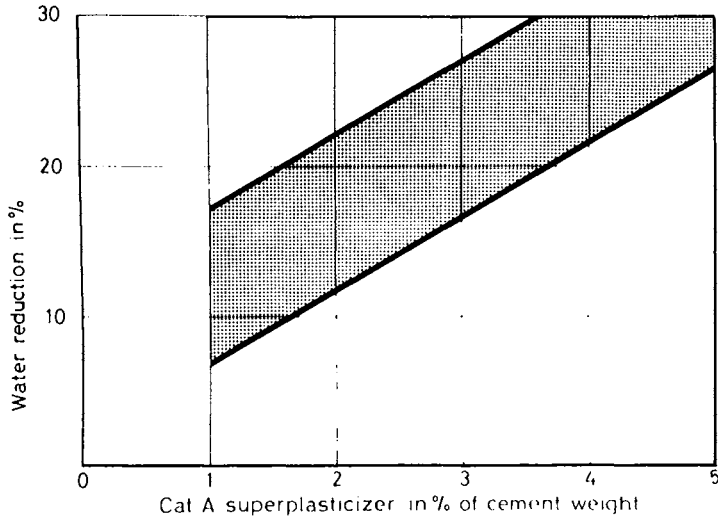


Fig. 5--Relation between water reduction and dosage of Category A superplasticizer

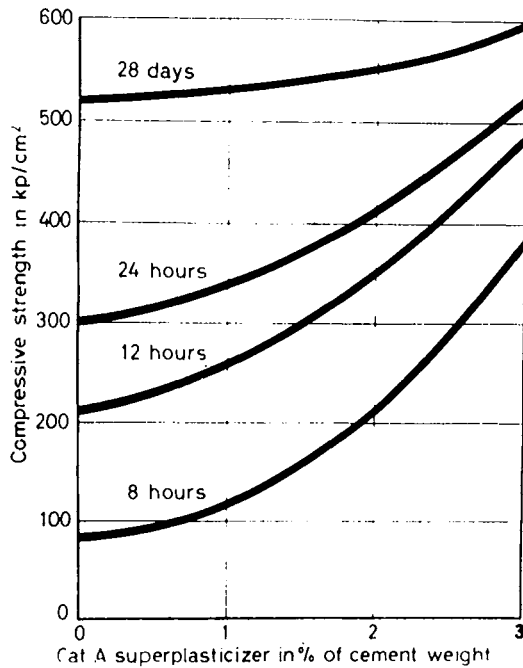


Fig. 6--Relation between compressive strength after 8, 12, and 24 hr, and 28 days; and concentration of Category A superplasticizer

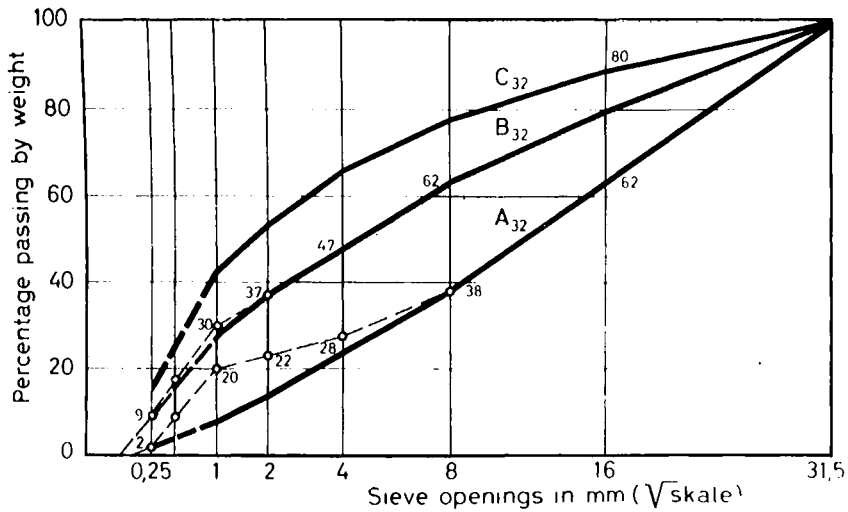


Fig. 7--Recommended grading limits for flowing concrete

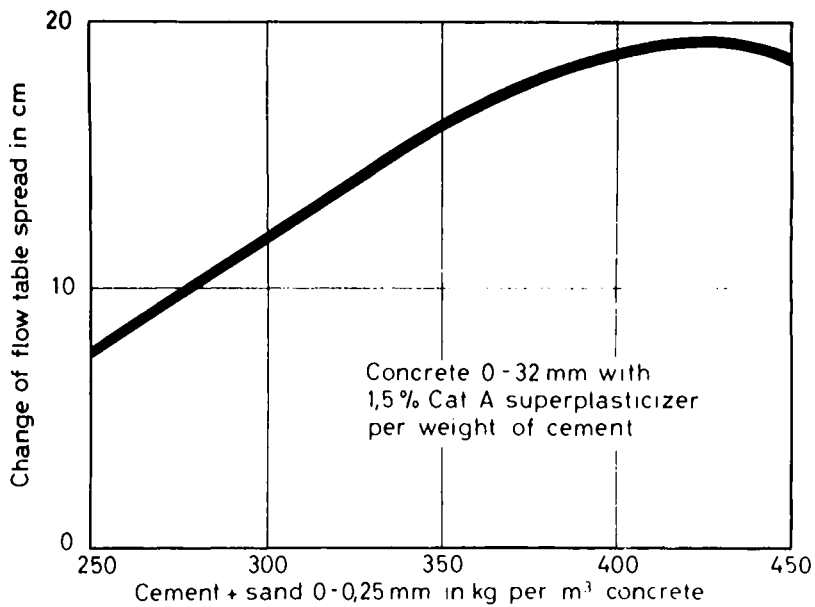


Fig. 8--Relation between change of flowtable spread and the content of cement and fine aggregate

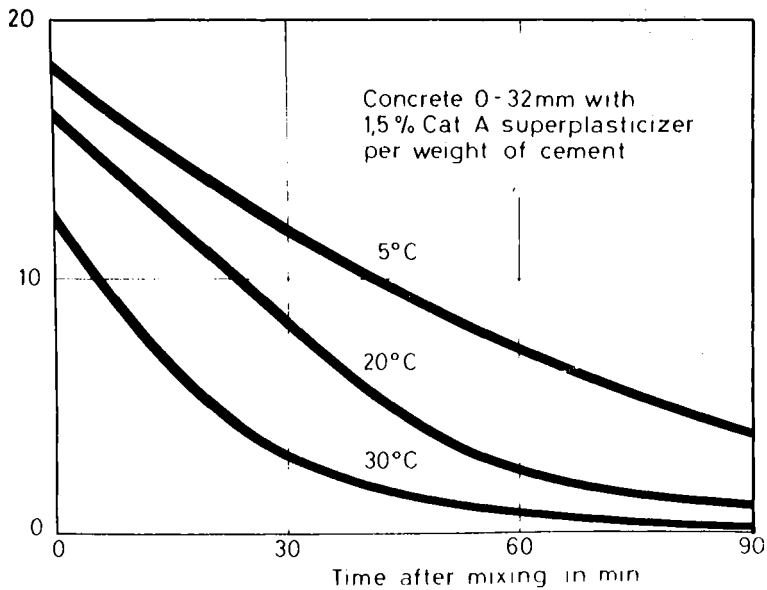


Fig. 9--Relation between change of flowtable spread and time; temperature of concrete 5, 20, 30 C

Experiences with Mighty Superplasticizer in Japan

By KENICHI HATTORI

Synopsis: In this paper, the author reports on the 14 year's experiences in Japan with formaldehyde high condensate of beta-naphthalene sulfonate (beta-NSFHC) which later became known as Mighty, since its commercial advent in 1964. The subjects described in this paper are as follows:

- 1) Brief history of the invention and the development.
- 2) Mechanism of dispersing cement particles by beta-NSFHC.
- 3) Production of high strength concrete by the use of beta-NSFHC.
- 4) Physical properties of high strength concrete thus produced.
- 5) Durability of concrete containing beta-NSFHC.
- 6) Biological safety.
- 7) Examples of the field practice of high strength and flowing concrete.

Keywords: admixtures; concrete construction; concrete durability; creep properties; drying shrinkage; freeze-thaw durability; fresh concretes; high-strength concretes; mechanical properties; modulus of elasticity; naphthalene compounds; physical properties; plasticizers; Poisson ratio; thermal expansion; toxicity; viscosity; water-cement ratio; water-reducing agents; workability.

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INTRODUCTION

Since 1958, the author has done an extensive basic study (1) on formaldehyde condensates of beta-naphthalene sulphonates. Based on this knowledge, it was discovered in 1962 that its high condensate was exceptionally effective for dispersing cement particles in water in comparison with other existing surfactants (2). The high condensate produced a very high flowability in fresh concrete, with a low tendency for set retardation and reduction of air-entrainment.

With increasing dosage of the condensate, the flowability of fresh concrete is improved to a much higher extent than with lignin type dispersants, resulting in the higher water reducing performance necessary for the production of high strength concrete (3-5).

By the early 1960's, most of the favourable properties of the high condensate as a superplasticizer for concrete were understood. In 1964, the product was first introduced into market by Kao Soap Company in powder and 42 wt. % active solution forms. During the past 14 years since its debut in the Japanese market, about 25 million cubic meters of concrete admixed with beta-NSFHC has been produced mainly in factory-prefabricated products and to a lesser extent, in site-placed structures.

By the introduction of beta-NSFHC, concrete products of 100 N/mm² (1000 kg/cm²) compressive strength at 28 days became commercially available in Japan. In 1965, centrifugally formed and autoclave-cured concrete piles with 70 N/mm² strength were first commercialized (6). In 1970, the world's first commercial production of autoclave-cured high strength concrete piles (7) with 90 N/mm² strength started in Japan. Application of high-strength concrete became popular very rapidly, and the field of application was extended to the construction of long-span railway bridges (8-11).

In 1971, the author and his co-workers developed a technique of controlling slump-loss during the delivery of ready-mixed concrete by the intermittent addition of beta-NSFHC (12). By this technique, site

placing of high strength concrete of low water-cement ratio (W/C) was made practicable. In the flowing concrete, recently developed in Germany (13), beta-NSFHC has been proven to be one of the most efficient plasticizers (14).

In Japan, particularly, the frequent use of pumping requires concrete of high fluidity. Without a suitable flowing aid, the requirement for water is high which tends to increase the probability of cracking through drying shrinkage. Under such circumstances, the property of beta-NSFHC as a powerful flowing aid is attracting keen attention as a means of controlling cracks. At the same time, flowing concrete is attracting attention as a technique of reducing corrosion of reinforcement in the concrete prepared from sea sand, due to its low water content and improved compactness.

In the following sections, the mechanisms of dispersing cement particles by beta-NSFHC, the physical properties of high strength concrete, the durability and examples of the structures and concrete products containing beta-NSFHC, and some results of a study to confirm the biological safety of beta-NSFHC are presented.

MECHANISM OF DISPERSING CEMENT PARTICLES BY BETA-NSFHC

It is generally known that the viscosity of cement paste is lowered when a dispersant is added. The decrease in viscosity occurs due to electric repulsion between particles absorbing the dispersant molecules. By adsorbing dispersant molecules onto cement particles, the agglomerates dissociate into primary particles. This concept has been accepted widely, but little has been reported on the proof on the thick cement paste.

It may be difficult to apply DLVO theory to cement paste strictly, mainly because of the solubility of cement and the complex molecular structure of the dispersants, but assuming that the particles are in the so-called "dormant stage", then the dispersion may be treated as a kind of hydrophobic colloid such as in the case of pigments.

As shown in Figure 1, the amount of adsorbed beta-NSFHC increases to about 5 mg/g cement, as the equilibrium concentration of beta-NSFHC in solution reaches approximately 0.8 per cent, after that the rate of increase falls off showing that the surface is nearly saturated.

Figure 2 shows that the zeta-potential of the cement particle without beta-NSFHC is +9.7 mV, and by the addition of small amount of beta-NSFHC, it starts to fall off sharply to about -15 mV. As the equilibrium concentration approaches 0.8 per cent, the zeta-potential reaches a negative maximum of -34 mV.

In Figure 3, the apparent viscosity of the cement paste measured with the Brookfield viscometer is shown. The decrease in viscosity is

almost inversely proportional to the equilibrium concentration until it reaches approximately 0.8 per cent, and stays constant afterwards. All the data in Figures 1 to 3 were obtained on cement pastes of 0.5 W/C ratio, into which beta-NSFHC was added at various concentration followed by 3 minute mixing. All the data show that sharp changes in physical properties and in electro-chemical behaviour occur at close to an equilibrium concentration of 0.8 per cent, which is equivalent to 0.9 per cent by weight of cement. Thus, it is verified that the viscosity reduction in the cement dispersion caused by beta-NSFHC arises from electrostatic repulsion. The decrease of yield value and plastic viscosity of the paste with increasing amounts of beta-NSFHC have been reported by Nagataki et al. (15), and it is clearly understood that the decrease in both rheological factors is due to the electrostatic repulsion.

Actually, beta-NSFHC can afford a fairly large flowability to the cement paste of 0.25 W/C ratio, which is approximately a theoretical water requirement for the hardening of cement. Thus, it is easily inferred that concretes containing such flowable cement paste are also flowable. The high flowability (16) manifested by beta-NSFHC is illustrated in Figure 4, and plates 1 and 2.

PRODUCTION OF HIGH STRENGTH CONCRETE ADMIXED WITH BETA-NSFHC

Japan's first ultra high strength concrete with compressive strength at 28 days of more than 100 N/mm² was experimentally produced by Yoshida (17) in 1940. Concrete employed was dehydrated to 0.23 W/C ratio under a pressure of 10 N/mm², and cured under high pressure and temperature. Since his success, the production of ultra high strength concrete has been a major target for scientists and technologists concerned with concrete technology. Shortly after the introduction of beta-NSFHC, technical papers concerning the production of ultra high strength concrete from mixes containing beta-NSFHC using standard curing (18) and autoclave curing (8) appeared, and commercial production started at nearly the same time.

Advantages of High Strength Concrete

Advantages of high strength concrete employing beta-NSFHC are summarized as follows (6-11,19):

- 1) Higher design strength can be obtained.
- 2) Larger prestress can be introduced in high strength concrete, and destruction of concrete products during the delivery and handling can be avoided.
- 3) The large water reduction produced by beta-NSFHC accelerates the hardening of concrete and can facilitate early introduction of prestress.
- 4) With the high strength, the cross section of elements of the

structure can be reduced. Reduction in the cross section results in the reduction of the dead load of a structure, which is favourable for tall buildings, long-span bridges, and for stability against earthquakes. The reduction also contributes to economical design of various structures without sacrificing good properties of concrete.

- 5) For a railway bridge, concrete is more effective than steel in eliminating the noise of train-running.
- 6) Due to its chemical stability, much less maintenance is required for concrete bridges than for steel bridges, and the durability is better with less maintenance.
- 7) Improved workability as well as low W/C ratio brought by the use of beta-NSFHC improves water-tightness of concrete.

Methods of Producing Ultra High Strength Concrete

The following three methods are applicable to the production of ultra high strength concrete.

- 1) The dehydration method applied by Yoshida which has already been mentioned.
- 2) The addition of silica powder at about 30 to 40 per cent weight of cement into the mix, followed by the curing in autoclave for much easier formation of tobermorite.
- 3) Reducing the W/C ratio as low as possible by the use of water reducers.

Method 3) seems the most practicable among the three methods mentioned above, and non-air entraining and non-retarding type water reducers are required for this purpose. Beta-NSFHC satisfies all the requirements for method 3) and is also effective in reducing or eliminating silica in the case of method 2).

As is seen in Table 1, 10 per cent of water reduction is given by both beta-NSFHC and lignin sulfonate at the normal dosage of 0.25 per cent as active without causing any retardation. In case of lignin sulfonate, at the dosage of 1.0 per cent, which is four times as high as normal, a 16 per cent reduction of water is obtainable, but the concrete does not harden within a week. For this reason, lignin sulfonate is not suitable for the production of ultra high strength concrete. On the contrary, beta-NSFHC can safely be mixed in the concrete at levels as high as 1.0 per cent, and very high water reduction rates, as high as 33 per cent, can be achieved.

The relationship between 28 day strength of concrete containing 400 to 600 kg/m³ of cement, and W/C ratio is shown in Figure 5 (20), the regression equation for the data is:

$$\sigma_{28} = 25.2 \text{ C/W} - 5.6 \text{ (N/mm}^2\text{)} \quad \dots (1)$$

From equation (1), the possibility of obtaining ultra high strength concrete of 100 N/mm² at a W/C ratio of 0.25 (C/W = 4) is indicated. One type of aggregates available in Japan was used to obtain the

results of Figure 5. With proper selection of aggregates and/or the use of high cement content, the line of correlation will shift parallel to the direction of high strength.

PHYSICAL PROPERTIES OF HIGH STRENGTH CONCRETE

High strength concrete is obtainable for a variety of mixes in a fairly wide range of mix proportion. The actual range of mixes for high strength concrete of 50-150 mm slump is: cement content of 500 to 700 kg/m³, W/C ratio of 0.2 to 0.3, S/A of 30 to 42 per cent, and beta-NSFHC of 0.6 to 0.9 per cent as active by weight of cement. These highly water-reduced concretes containing beta-NSFHC can be placed easily with vibration. Although the workable time of concrete containing beta-NSFHC is shorter than that of plain cement, it can be extended by intermittent addition of beta-NSFHC (12) as already mentioned.

To produce ultra high strength concrete of more than 100 N/mm² at the site is not easy due to the limited availability of suitable aggregates which is the most important material.

To investigate the physical properties of high strength concrete, a series of formulations in a wide range of W/C ratio of 0.25 to 0.55, having the same slump of 100 mm, same paste volume of 29 per cent, and constant S/A ratio of 0.43 were prepared by changing the dosage of beta-NSFHC. A number of properties of concrete for these mixes have been examined under the cooperative program between Kao Soap Company and Japan Testing Centre for Construction Materials (21).

Strength Data

Strength data and mix formulations are shown in Table 2, and strength data as a function of W/C ratio are shown in Figure A of the appendix. From Table 2, the contribution of low W/C ratio to the high strength after 1 day increased progressively with decreasing W/C ratio, thus attaining the maximum 1 day strength of 47.2 N/mm² at 0.25 W/C ratio. Twenty eight day strength of 110.8 N/mm² obtained for the formulation of 0.25 W/C ratio was the highest among the values ever reported.

In Table 3, flexural strength, tensile strength, and maximum bond strength in relation to compressive strength and W/C ratio are shown. Actual strengths were higher for the concretes of lower W/C ratio. The flexural and the tensile strength of concrete of 0.25 W/C ratio after 28 days rated 10 per cent and 6 per cent to the value of the compressive strength, which were slightly smaller than those of plain concrete of 0.55 W/C ratio, 12 and 8 per cent, respectively. Decreasing with the lowering of W/C ratio, the ratio of the maximum bond strength to the compressive strength were 50 per cent and below 30 per

cent in the cases of plain concrete and the high strength concrete, respectively.

Static Modulus of Elasticity and Poisson's Ratio

Relationships between compressive strength and static modulus of elasticity, and compressive strength and Poisson's ratio are shown in Figure 6. The modulus of concrete of 0.25 W/C ratio was 41.8 kN/mm^2 which was lower than the expected value of 54.9 calculated from the equation of ACI standard (22). The modulus increased linearly as the compressive strength increased to about 100 N/mm^2 , whereas the Poisson's ratio increased with increasing compressive strength, via a fairly wide plateau region ranging between 40 to 90 N/mm^2 .

Drying Shrinkage

As shown in Figure 7, drying shrinkage up to 28 days was the highest for concrete of 0.4 W/C ratio among the mixes tested. For concrete of 0.40 to 0.55 W/C ratio, effect of water reduction to reduce drying shrinkage between 6 to 12 months of age did not appear clearly because, increased cement content, 300 to 400 kg/m^3 masked the effect. For concretes of 0.25 to 0.4 W/C ratio, the effect of water reduction was larger than that of increased cement, 400 to 500 kg/m^3 , and a fairly low value of 5×10^{-4} was obtained for concrete of 0.25 W/C.

Coefficient of Creep

As shown in Figure 8, coefficient of creep and specific creep decreased as the compressive strength increased. This is the same trend as reported by Neville (23) and Nagataki (24). Nagataki (24) also found that the specific creep/unit paste volume of the concrete decreased linearly as the compressive strength of concrete increased. According to our researches, specific creep of high strength concrete (0.25 W/C ratio) was $2.62 \times 10^{-5} \text{ mm}^2/\text{N}$, and the coefficient 1.12 , which were about one third of those of ordinary plain concrete respectively. This property of the high strength concrete is considered to be favourable for the production of prestressed concrete.

Thermal Expansion

The coefficient of thermal expansion of concrete decreased as the water content of concrete increased, as shown in Figure 9. Free water in the concrete was considered to reduce the coefficient. When free water in the specimens of concrete which have 0.25 to 0.55 W/C

ratio was removed by drying at 105°C, the coefficient of each specimen was in a very narrow range of $1.0 - 1.2 \times 10^{-5}/^{\circ}\text{C}$.

DURABILITY

Freezing and Thawing Resistance

It is generally accepted that expansion of free water in concrete on freezing causes its destruction. This concept leads to conjecture that the elimination of free water in concrete is one of the ways to improve resistance of concrete to freezing and thawing. For non-air entraining concretes, satisfactory resistance at 300 cycles was reported by Goto (25) at 0.26 W/C ratio, by Kobayashi (26) at 0.3 W/C ratio, and by Saito (8) at 0.35 W/C ratio, but, Goto's report (23) was negative for the concrete of 0.33 W/C ratio. From these reports, it is suggested that the resistance is satisfactory for non-air entraining concrete if W/C ratio is lower than 0.3. For concretes of W/C ratio higher than 0.3, air entrainment is recommended to improve freezing and thawing resistance.

Freezing and thawing resistance of concretes containing beta-NSFHC with and without air entraining agent (resin soap) is shown in Table 4 and large improvement in the resistance due to incorporation of air entraining agent is also shown. Higher dosage of resin soap than normal is usually required when it is used in combination with beta-NSFHC, though the results in Table 4 did not show such tendency.

At the higher dosages of beta-NSFHC, the bubble spacing factor of concrete containing beta-NSFHC and resin soap, exceeds 0.2 mm which is considered as the upper limit for satisfactory freezing and thawing resistance of concretes. Notwithstanding above, the resistance to freezing and thawing of concrete was satisfactory. The author and his co-workers have found several additives which when used as air-entraining agents in combination with beta-NSFHC, improve the freeze-thaw resistance of concrete by entraining 4 to 5 per cent air and maintaining the bubble spacing factor lower than 0.2 mm.

Durability of 11 Year Old Buildings (27)

Table 5 shows test results of cores taken from the wall and the floor of an 11 year old building. Comparison of compressive strengths at 28 days and at 11 years confirms that the increase in strength continues for much longer than 1 year. Normal crystal growth in the cores at 11 years was also confirmed by X-ray diffraction patterns.

Corrosion of Reinforcement in Five Year Old Piles (28)

To investigate the influence of the admixtures and calcium chloride on the rusting and corrosion of reinforcement, test piles were prepared from mixes containing admixtures and calcium chloride by centrifugal forming under prestressing, followed by curing in steam and autoclave. The dimensions of test piles were, 300 mm outer diameter, 70 mm wall thickness, and 2300 mm in length having four steel rods per pile as reinforcement. The test piles were cured in water for a year and then left outdoors for 4 years. Five years after the preparation of the test piles, the reinforcements were taken out for the evaluation of rusting. The results are shown in Table 6.

No rust was found on reinforcements, regardless of the admixture formulations, after one year curing in water. After five years reinforcements in piles containing high dosages of calcium chloride exhibited heavy rusting but few rust spots were found in those piles which did not contain calcium chloride. In the case of calcium chloride, the area of rusting was almost proportional to the dosage of calcium chloride. The rusting occurred mainly on the side of the reinforcement facing the outside. This side of the reinforcement is considered not to adhere well to concrete on account of negative pressure caused by centrifugal force.

As is seen in Table 6, no harmful effect of the gap formation appeared for plain concrete or concrete containing beta-NS HC or lignin type but without CaCl_2 . It is highly probable that even a small amount of calcium chloride is very harmful on the long term durability of concrete structures containing steel reinforcement if narrow gaps and cracks reach the reinforcement.

Confirmation of Biological Safety

Biological safety of beta-NSFHC has been and is being examined. Following is a brief summary abstracted either from our own tests or from the experiments sponsored by the Kao Soap Company.

- 1) Acute toxicity: $\text{LD}_{50} = 5 \text{ g/kg}$ by rat and mouse.
- 2) Chronic toxicity (29). Maximum permissible dose was about 100 mg/kg day by the six month test using rat.
- 3) Fish toxicity: TLM_{50} for gold fish was larger than 500 ppm which was much safer than toilet soap. About same level of the toxicity was found for other species of fishes.
- 4) Three generation reproduction studies, teratogenic studies, and carcinogenic studies are now under progress, and an interim report indicated no abnormality or severe toxicity.
- 5) Not very high biodegradability of 5 per cent in a week was found.

EXAMPLES OF APPLICATION OF CONCRETE CONTAINING BETA-NSFHC

Application in High Strength Concrete

Although most of the demand for beta-NSFHC in the early years after commercialization has been for factory made concrete products, but taking advantage of the capability of beta-NSFHC to produce high strength concrete, many important structures have been constructed using concrete containing beta-NSFHC. Names and the dates of construction of the structures are listed in Table 7, and information on the mix formulations is shown in Table 8.

Applications in Flowing Concrete

Applications of flowing concrete technique in construction practice started only recently in Japan. Due to the improvement in flowability and reduction of water content, the popularity of flowing concrete is expected to increase rapidly in the near future. In a short span of two years, many construction works in Japan such as buildings especially those using tile-fixed frames, a baseball stadium, a dam, silos, and towers, have been completed applying beta-NSFHC as a superplasticizer. The non-retarding and non-air entraining properties of beta-NSFHC are considered very important in this regard.

Two typical examples of the formulation of base concrete in construction applying flowing concrete technique in combination with beta-NSFHC are shown in Table 9.

Other Applications

In addition to the applications mentioned above, beta-NSFHC has been and is used in many concrete elements such as beams, sleepers, railway slabs for the Shinkansen, box culverts, prefabricated panels, pipes, gathering places for fish, and etc. Recently beta-NSFHC has also been used in the production of glass fiber - and steel fiber - reinforced concretes. Applications in various kinds of marine structures are expected in the future.

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TABLE 1

Effect of Dispersing Agents on Properties of Concrete

Dispersant	Dosage (% wt. of cement)	W/C	Water reduction rate (% wt.)	Slump (mm)	Air Content (% vol.)	Compressive strength (N/mm ²)		
						at 3 days	at 7 days	at 28 days
Plain	0	0.39	0	57	0.8	18.8	33.6	41.6
Beta-NSFHC (Powder) (S/A=36.3 % vol.)	0.25	0.35	10	57	1.1	23.6	38.1	45.1
	0.50	0.31	20	47	1.3	31.6	46.2	56.3
	0.75	0.273	30	112	1.6	46.3	58.0	75.3
	1.00	0.26	33	44	1.7	44.8	53.4	73.8
Calcium lignin sulfonate (S/A=34.3 % vol.)	0.25	0.35	10	46	3.1	25.8	37.3	48.4
	0.50	0.34	12	71	7.2	26.9	41.9	50.9
	0.75	0.329	15	91	8.6	not hardened	18.8	44.3
	1.00	0.327	16	64	10	not hardened	not hardened	33.8

Cement Type: Asano Ordinary Portland Cement

Cement Content: 440 kg/m³

TABLE 2

Effect of Water-Cement Ratio on Compressive Strength

Water/Cement	0.55	0.50	0.45	0.40	0.35	0.30	0.25
Sand/Aggregate*, % vol.	43.0	43.0	43.0	43.0	43.0	43.0	43.0
Cement**, kg/m ³	334	355	378	404	434	471	512
Water, "	185	178	171	162	153	142	128
Beta-NSFHC (42% solution) (% wt. of cement)	---	0.7	1.0	1.4	1.8	2.2	2.95
Slump***, mm	93	96	94	97	96	106	108
Air, % vol.	1.2	1.2	1.4	1.5	1.5	1.5	0.8
Compressive Strength**** (N/mm ²)							
1 day	11.4	12.9	17.6	19.7	29.6	41.5	47.2
3 day	21.1	31.0	36.9	45.6	61.6	74.0	82.6
7 day	32.3	42.8	51.0	59.0	75.1	85.3	93.8
28 day	41.6	52.7	58.5	70.0	85.6	96.6	110.8
365 day	49.6	60.8	72.8	85.8	100.2	112.8	120.6

*739 kg sand and 1044 kg gravel were used for all formulations
to make the paste volume constant

**Chichibu high early strength Portland cement

***Target slump, 100 ± 10 mm

****Test specimens were cured in water of 20°C before measurements

Note: specimen size = 100 x 200 mm cylinder cement paste
volume = 29.1%