CHAPTER 1

SUPERPLASTICIZERS
INTRODUCTION AND LITERATURE SURVEY

1.1 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 lead to the development of superplasticizers (High range water-reducing admixtures). In Japan, Hattori and co-workers (1979) pioneered the development of formaldehyde condensates of beta-naphthalene sulphonates 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 plasticizer. 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 (1981) used 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 for the Montreal Olympic stadium.

Superplasticizers may be classified into the following four categories:
A. Sulphonated melamine-formaldehyde condensate
B. Sulphonated naphthalene-formaldehyde condensate
C. Modified lignosulphonates
D. 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 superplasticizer may vary from less than 100 to 100,000.

1.2 TYPES OF SUPERPLASTICIZERS

Several distinct types of superplasticizers are available, based on different chemicals, although they purport to have a similar function in concrete. They are all organic compounds of high molecular weight, some being synthetic and others derived from natural products.

Categories of superplasticizer:

A. Sulphonated melamine-formaldehyde condensates: These are polymers with the value of \( n \) (the condensation number) usually in the range 50-60, giving a molecular weight in the region of 20,000.

B. Sulphonated naphthalene-formaldehyde condensates: These are polymers similar in many ways to the previous category, with a simple repeating unit. Again sodium salt is usually employed, solubility being due to the sulphonate groups. The value of \( n \) in this case is typically in the range 5-10, giving a molecular weight of the order of 2000.

C. Modified lignosulphonates: The crude lignosulphonates derived from wood-pulp are commonly used as plasticizers, and in order to improve their effectiveness they can be refined and modified.
The processing involves the removal of sugars and other impurities, selection of a higher molecular weight fraction and, optionally, further sulphonation or partial polymerisation. The calcium or alkali metal salts are employed in the admixture, the latter having superior water-reducing capability. The basic repeating unit of the lignosulphonate molecule has a complex phenyl-propane skeleton. Substituent groups vary and may include phenolic, carboxylic and methoxy substances in addition to sulphonate. In solution, the molecule coils into a spherical configuration, with anodised groups at or near the surface.

D. Various chemicals or mixtures, which are claimed to act as superplasticizers: Acid amide/polysaccharide mixtures and other high molecular weight hydroxylated polymers and co-polymers are examples. This is not a very important category as yet, but current research could give rise to new types of superplasticising admixtures in the near future. In recent years the discussion between these categories has become rather blurred, as attempts have been made to blend B and C materials in order to produce a cheaper but effective superplasticizer. Also a new class of 'retarding superplasticizer' has gained acceptance for applications where a longer retention of high workability is required. These are usually a blend of retarding plasticiser and category A and B superplasticizer, and is covered by BS 5075: part 3. They are already included in the ASTM C-494 specification.

1.3 MODE OF ACTION

As a group of materials water-reducing agents are characterised by having detergent like properties. These we call surface activity, and the materials surface-active agents. They carry an unbalanced charge of electricity
and if put into water tend to migrate to the surface with the electrically-charged or active end sticking into the water, whilst the 'tail' is out in the air (figure 1.1). If we now put a surface active agent into a suspension of cement particles in water two things happen:

01. The surface-active agent's 'tail' is adsorbed onto the surface of the cement with the negative charge protruding into the water. As a result, the cement particles do not collect together and therefore more surface area is available for reaction with the water. At the same time water that may have been trapped inside a cement particle floc is released. The combined effects, shown in figure 1.2, improve the workability and mobility of the mix.

02. Entrapped air is also more readily removed since orientation of the surface-active agent prevents the air bubble from attaching to cement particles, as shown in figure 1.3.

Plasticising water reducers, due to their ability to migrate to the water/air boundary, reduce the surface tension at the boundary and can form very stable air bubbles. This is the principle behind air-entraining agents.

However, in plasticizers this tendency can be offset by introducing an air-detraining agent.

If the concrete is being made to a given workability, say slump value, then the addition of water-reducing agent gives rise to the following possibilities:

01. Concretes having greater workability may be made without the need for more water and so strength losses are not encountered. (Table 1.1a compare SI.No. 1 and 2)
Figure 1.1 - Migration of water-reducing agents to surface of water
Figure 1.2 - Effect of Surface Active Agent on Cement particle floc
Figure 1.3 - Repulsion of Air Bubble by Surface Active Agent
02. By maintaining workability, but at a lower water content, concrete strengths may be increased without the need for further cement addition. (Table 1.1a compare Sl.No. 1 and 3)

03. Whilst maintaining the water:cement ratio and workability, concrete can be made to a given strength specification at lower cement contents than would otherwise be possible.

Table 1.1a Purposes achieved by use of water-reducing agents

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Test</th>
<th>Cement content Kg/M³</th>
<th>Dosage rate</th>
<th>W/C ratio</th>
<th>Slump (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control</td>
<td>375</td>
<td>-</td>
<td>0.47</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Superplasticized</td>
<td>375</td>
<td>1%</td>
<td>0.42</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>Superplasticized</td>
<td>375</td>
<td>1.5%</td>
<td>0.40</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>Superplasticized</td>
<td>375</td>
<td>2.5%</td>
<td>0.39</td>
<td>55</td>
</tr>
</tbody>
</table>

Water-reducing agents can give benefit in concrete containing harsh and/or poorly graded aggregates and for concrete being placed under difficult conditions such as using a Tremie.

In order to recoup the benefit of using a water-reducing agent, care must be taken in controlling the air content of the mix. Most water reducing agents entrain air due to their surfactant properties. This can be offset by including in this type of admixture an air-detraining agent such as tributylphosphate. See Table 1.1b.
Table 1.1b Use of an air-entraining agent with a water-reducing agent

<table>
<thead>
<tr>
<th>Admixture</th>
<th>Dosage (%)</th>
<th>Slump (mm)</th>
<th>Air content (%)</th>
<th>Water reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>89</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Lignosulphonate</td>
<td>0.16</td>
<td>89</td>
<td>3.8</td>
<td>11.3</td>
</tr>
<tr>
<td>Water-reducing agent (unmodified)</td>
<td>0.26</td>
<td>114</td>
<td>5.0</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>114</td>
<td>6.5</td>
<td>17.9</td>
</tr>
<tr>
<td>Lignosulphonate</td>
<td>0.16</td>
<td>102</td>
<td>2.5</td>
<td>5.8</td>
</tr>
<tr>
<td>Water-reducing agent (modified)</td>
<td>0.26</td>
<td>89</td>
<td>3.3</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>102</td>
<td>3.8</td>
<td>12.8</td>
</tr>
</tbody>
</table>

1.4 TYPES OF MATERIALS

01. Lignosulphonate salts

These are naturally occurring materials which are obtained by pulping wood, using lime and sulphurous acid mixture. They are usually described as calcium lignosulphonates although sodium, ammonium and magnesium are also available and may or may not contain a proportion of sugars. If sugars are present retardation may occur; alternatively, a refined, sugar-reduced product may be used which avoids excessive retardation.

02. Polyhydroxy compounds (carboxylic acid based)

These materials are similar in function to the lignosulphonates and may be sensitive to over-dosing leading to excessive retardation.

03. Superplasticizers

A new range of plasticising admixtures is now available based on synthesised condensates. Such materials as a group could be specified as
formaldehyde derivatives such as sulphonated melamine-formaldehyde and naphthalene sulphonate-formaldehyde. These materials have a remarkable plasticising action, producing slumps in excess of 200 mm with no increase in water content. Alternatively, water reductions as high as 30% may be achieved.

This plasticising effect is being used both in the continent and to some degree in the USA and Japan for projecting the concept of 'fluid' or 'soapy' concrete. The disadvantage of these materials is their high basic cost, although each product should be judged on the basis of its cost-in-use. It is worth mentioning that chemicals capable of imparting high fluidity to a concrete should also avoid bleeding and segregation in order to be totally effective.

The mechanism by which superplasticizers produce their effect is very similar to that of normal plasticizers. The main difference is that the former consists of very large molecules (colloidal size) which dissolve in water to give ions with very high negative charge (anions). The configuration of the anions is not known (except in the case of lignosulphonates). However, in the sulphonate groups, the anions are oriented outwards from the water surface. These anions are attracted to the surface of cement grains and, at the normal levels of admixture usage, are adsorbed in sufficient numbers to form a complete monolayer around them.

The combination of electrostatic repulsion and large ionic size (which provides physical separation) brings about a rapid dispersion of the individual cement grains. In doing so, water trapped within the original flocs is released and can then contribute to the mobility of the cement paste - and hence to the workability of the concrete.

Superplasticizers do not cause much reduction in the surface tension of water, hence there is little tendency to excessive air entrainment even at
high dosage. The adsorption of the anions on the surface of cement grains is also less tenacious than in the case of retarders (e.g. hydroxy carboxylic acid salts) and the course of hydration reactions is not hindered at normal dosage levels. Hence, for normal superplasticizers, there should be no significant retardation of setting and hardening.

With retarding superplasticizers there will, of course, be a degree of retardation depending on the dosage employed.

1.5 EFFECT OF FRESH CONCRETE MIXED WITH SUPERPLASTICIZERS

The properties of fresh concrete containing a superplasticizer are affected by both the category of the superplasticizer and by the initial workability of the mix. It is, therefore, convenient to compare the properties of a control mix with those of a superplasticized mix which has been water-reduced to give equal workability and also with a mix of unchanged water content which will produce a high workability leading to flowing concrete.

When used as a high range water-reducer to produce high strength concrete, normal mix design procedures are used. In this mode of use the full potential of the admixture as a water reducer is not realised if the mix is over cohesive and particularly with category C superplasticizers. This can retain up to 1.5% additional air and some reduction in sand content will be possible and desirable.

It should be noted that due to high levels of water reduction workability may be lost rather more quickly than would be expected with a normal concrete mix of the same workability.
When the superplasticizer is used to produce flowing concrete the effect on the cohesion of the mix can be significant, particularly at the highest end of the flowing range. A mix which appears cohesive at a slump of 100 mm may, when superplasticized, show considerable segregation of the coarse aggregate during placing and bleed. These undesirable properties can be avoided by careful choice of superplasticizer type, mix design, aggregate shape and grading.

Category C superplasticizers, because of their tendency to slightly increase air entrainment, may enhance the cohesion of the mix. Category B generally have little effect on air, while category A usually reduce the natural air entrainment, thereby slightly reducing the cohesion. These factors should be borne in mind when selecting the superplasticizer category especially if changes in mix constituents are not feasible for producing a good cohesive mix.

The choice of the time of addition of superplasticizer depends partly on which category of the superplasticizer is used since the retention of high workability may be relatively short-lived, particularly with category A.

The traditional methods of slump and compacting factor are generally inappropriate for measuring the workability of flowing concrete. Slumps are normally in excess of 200 mm and in a range which lack sensitivity and no longer gives a meaningful correlation.

Flow can be measured on a standard flow table (detailed in BS 1881 part 105) and has been found to be an appropriate method of assessing the workability of flowing concrete. Concrete is regarded as flowing when the diameter of spread, measured on the flow table, exceeds 510 mm. At values in excess of about 620 mm, concretes containing category A and B superplasticizers may become prone to bleed and segregate. However with proper mix design with category C superplasticizers satisfactory results can
be achieved at flow values in excess of 650 mm, mainly because of their enhanced cohesion.

The dosage required to give a particular level of fluidity is dependent on the category of the superplasticizer, the concrete mix design and its constituents. It should not be assumed that a superplasticizer which gives satisfactory flowing concrete on one mix will, at the same dosage, do so on another mix using a different sand or aggregate.

For a given application, the period over which it is desirable for a superplasticizer to retain its fluidity will depend on several factors. These include ambient temperature, likely time delay between the addition of the superplasticizer and placing of the concrete, and time delays to subsequent pours if self-compaction is required or the time for preferred access on the still plastic concrete required for topping the surface.

Different categories of superplasticizer generally retain their workability for characteristic periods, though further modifications of the admixture by manufacturers can alter the situation. The flow value retention period is significantly affected by the initial workability of the mix.

At high levels of workability the stability of entrained air is low and the use of a superplasticizer usually results in a reduction of up to 0.6% in the level of naturally entrained air. Category A superplasticizers produce the greatest tendency for air detrainment with typical reduction of 0.3 to 0.5%. Category C have the least effect and may even give a slight air entrainment. (-0.1% to +0.2%). The air entrainment of category B falls between those of category A and category C.

Those categories of superplasticizer which give extended periods of high workability will result in extended setting times. This needs to be borne
in mind when selecting the category of superplasticizer for a particular application especially when used at very low or at very high temperatures.

In water-reduced mixes a reduction in the entrained air over the control mix is unusual but does occasionally occur with the category A superplasticizers. They have a -0.2% to +0.2% effect on air entrainment. The corresponding effects for category B is 0.0 to +0.5% whilst for category C it is +0.5 to +1.5%. Air entrainment of superplasticized, water-reduced concrete using a conventional air entraining agent is straightforward but the air-entraining admixture should preferably be added after the superplasticizer.

Setting times of water-reduced mixes, having the same workability as the control mix vary from -30 minutes for category A superplasticizers to +60 minutes for category C, when compared with the setting times of control mix.

1.6 STANDARDS FOR SUPERPLASTICIZER

British Standard 5075: part 3 published in 1985, lays down performance and uniformity requirements for superplasticizers. The performance are based on flow and compressive strength values of superplasticized concrete at equal water content to a control mix of initial slump 75 +/- 10 mm. The standard also lays minimum and maximum limits on the time over which the workability may fall back to that of the initial control workability. In addition, the standard requires a mix in which the water is reduced to give equal workability with the control mix. Comparisons are then made between the control and test mixes for compressive strength and setting time. The standard covers normal and retarding types of superplasticizer and the performance requirements are summarised below and in Table 1.2 and 1.3.
BS 5075: part 3 performance test requirements are:

1. All tests are compared with a control mix having a nominal 75mm slump.

2. The air content of the control concrete shall be less than 2% and the test mixes containing the superplasticizer less than 3%.

3. Test Mix A contains the superplasticizer and has the same water content as the control giving a high workability flowing concrete.

4. Test Mix B contains superplasticizer and has the water content reduced to give equal workability as that of control mix.

Table 1.2 Performance requirements for flowing concrete - Test Mix A

<table>
<thead>
<tr>
<th>Property</th>
<th>Test method</th>
<th>Superplasticising</th>
<th>Retarding superplasticising</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>Flow table as per BS 1881: Part 105</td>
<td>510-620 mm</td>
<td>510-620 mm</td>
</tr>
<tr>
<td>Workability loss on standing, with respective to that of initial control slump</td>
<td>Slump to BS 1881 part 102</td>
<td>At 45 min: not less than initial control at 4 hrs. not more than initial control</td>
<td>At 4 Hrs.: not less than initial control</td>
</tr>
<tr>
<td>% compressive strength with respect to control</td>
<td>BS 1881 part 116</td>
<td></td>
<td></td>
</tr>
<tr>
<td>At 7 days</td>
<td></td>
<td>Not less than 90%</td>
<td>Not less than 90%</td>
</tr>
<tr>
<td>At 28 days</td>
<td></td>
<td>Not less than 90%</td>
<td>Not less than 90%</td>
</tr>
</tbody>
</table>
Table 1.3 Performance requirements for water reduced concrete - Test Mix B

<table>
<thead>
<tr>
<th>Property</th>
<th>Test method</th>
<th>Super plasticising</th>
<th>Retarding superplasticising</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slump relative to control</td>
<td>BS 1881: part 102</td>
<td>A maximum reduction of 15 mm</td>
<td>A maximum reduction of 15 mm</td>
</tr>
<tr>
<td>Stiffening time relative to control</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For 0.5 N/mm²</td>
<td>BS 4551</td>
<td>With in 1 hr</td>
<td>1hr-4hr longer</td>
</tr>
<tr>
<td>For 3.5 N/mm²</td>
<td>5075 test method</td>
<td>With in 1 hr</td>
<td></td>
</tr>
<tr>
<td>% compressive strength on control</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At 1 day</td>
<td>BS 1881: Part 116</td>
<td>Not less than 140%</td>
<td>-</td>
</tr>
<tr>
<td>At 7 days</td>
<td></td>
<td>Not less than 125%</td>
<td>Not less than 125%</td>
</tr>
<tr>
<td>At 28 days</td>
<td></td>
<td>Not less than 115%</td>
<td>Not less than 115%</td>
</tr>
</tbody>
</table>

The American Standard ASTM C 494 was extended to cover superplasticizers in 1980 and considers 2 types: type F normal and type G retarding. They are termed high range water reducers and are only tested in this mode. The range of tests suggested is wider and includes compressive strengths up to 12 months, flexural strengths, shrinkage and durability under conditions of freeze thaw cycles. The main performance requirements are given in Table 1.4.
Table 1.4 A summary of ASTM C494 performance test requirements for Superplasticizers

**Performance requirements**

<table>
<thead>
<tr>
<th>Property</th>
<th>Test method ASTM</th>
<th>Type F water reducing high range</th>
<th>Type G water reducing, high range and retarding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Setting time relative to control mix</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial 3.5 N/mm²</td>
<td>C403</td>
<td>1 hr earlier to 1.5 hr later</td>
<td>1 to 3.5 hr later</td>
</tr>
<tr>
<td>Final 27.5 N/mm²</td>
<td></td>
<td>1 hr earlier to 1.5 hr later</td>
<td>Not more than 3.5 hr later</td>
</tr>
<tr>
<td>% compressive strength with respect to control mix</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 day</td>
<td>C39</td>
<td>140</td>
<td>125</td>
</tr>
<tr>
<td>3 day</td>
<td></td>
<td>125</td>
<td>125</td>
</tr>
<tr>
<td>7 day</td>
<td></td>
<td>115</td>
<td>115</td>
</tr>
<tr>
<td>28 day</td>
<td></td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>6 months</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1 year</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>% Flexural strength with respect to control mix</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 day</td>
<td>C78</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>7 day</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>28 day</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>% Shrinkage relative C157</td>
<td>C157</td>
<td>135%</td>
<td>135%</td>
</tr>
<tr>
<td>Freeze/thaw durability C666 factor</td>
<td>C666</td>
<td>80%</td>
<td>80%</td>
</tr>
</tbody>
</table>

**Note:**
1. All tests are compared with a control mix having a nominal 75mm slump.
2. The air content of the control and test mixes shall be less than 3% and the control mix air content shall be adjusted to have an
1. Air content within +/- 0.5% of the test mix using a standard resin solution.

3. The superplasticized mix is only tested in a water reduced mode and shall give at least 12% water reduction at the same workability.

The development and use of superplasticizers has revolutionised 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 type of cements and supplementary cementing materials. Rapid methods to control quality of the superplasticizers are needed. (Malhotra, 1989).

1.7 WATER-REDUCED HIGH STRENGTH CONCRETE

As a result of the much improved workability that the addition of a superplasticizer gives to concrete made at a normal water/cement ratio, it is possible to make concrete having a slump = 50 to 75mm, but with a very much reduced w/c ratio. However, much of the development in the use of superplasticizers as water reducers has occured in Japan, where conventional workability is approximately 200 mm slump.
It is worth remarking that, in theory, a water/cement ratio of 0.27 is adequate for hydration of the cement, and any water in the concrete above this ratio reduces the potential compressive strength that can be achieved. For instance, the correct selection of cement, aggregate and curing conditions can yield concrete having a compressive strength of 96 N/sq.mm and a flexural strength greater than 11 N/sq.mm. It is therefore unfortunate that most common concrete placing practices demand a level of workability which cannot normally be obtained without addition of some, and often considerable water above the theoretical requirement thus lowering the strength. At a water/cement ratio of 0.30 or thereabouts, the workability of most concrete is impaired.

Increasing the cement content to achieve early high strength may result in excessive heat output, causing cracking as well as undesirable shrinkage. Cement increase alone is not as desirable as a reduction in water/cement ratio to achieve early high strength.

It is clear, therefore, that any means, consistent with good concreting practice, of reducing this ratio closer to the theoretical level is desirable. Superplasticizers are claimed to go some significant way towards satisfying this requirement, as water reductions in the region of 20 to 33% are obtainable by their proper use, although limited by grade of cement, aggregate and temperature. By comparision, water reductions of only 15 to 16% are obtainable with lignosulphonate-based plasticizers. Water-reduced concrete containing superplasticizers are noted for their high early and ultimate strengths, excellent durability and waterproofing characteristics.

The technique of producing low water/cement ratio concrete for the purpose of obtaining high strength or retaining workability at reduced water requirement was pioneered in Japan using a category B admixture. It is common practice in Japan to use over-sanded, high-slump concretes for
general construction, in order to resist earthquakes. When buildings contain large quantity of reinforcement, placing of conventional European type concrete is difficult. Superplasticizers are used to reduce the water requirement of such mixes while maintaining a 200 mm slump.

Around the year 1972 category A admixture began to find application in Germany and has since been used in France, Belgium and Italy. In 1974 interest was shown in this technique in the U.K, and it is estimated that during that year some 15,000 M³ of water-reduced concrete containing one or more of the listed superplasticizers was placed (Hewlett, 1977).

Properties of Fresh Concrete:

Table 1.5 gives data relating to concrete made at two fixed workabilities. The water content has been increased. The data relate to a nominal 1:2:4 mix containing 300 Kg/M³ of cement content mixes.

Table 1.5 The water-reducing capability of Superplasticizers

<table>
<thead>
<tr>
<th>Admixture dosage</th>
<th>W/C ratio</th>
<th>Water reduction(%)</th>
<th>slump (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>0.5%</td>
<td>0.57</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>1%</td>
<td>0.52</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>1.5%</td>
<td>0.48</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>0</td>
<td>0.55</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>0.5%</td>
<td>0.48</td>
<td>13</td>
<td>50</td>
</tr>
<tr>
<td>1%</td>
<td>0.44</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>1.5%</td>
<td>0.39</td>
<td>28</td>
<td>45</td>
</tr>
</tbody>
</table>

Such water reductions can yield noticeable increases in both early and ultimate strengths.
1.8 LITERATURE SURVEY

High strength concretes with a compressive cube strengths of 80-110 N/Sq.mm were studied by Parrot (1969) without use of admixtures. However while studying the properties of fresh and hardened concrete, the consistency of fresh concrete was rather low. It was then recognised that, by using a superplasticizer, more workable mixes can be achieved while permitting a high cement content and a low water cement ratio, both of which are necessary to obtain ultra-high strengths by conventional mixing techniques.

The properties of ultra-high strength concrete mixes containing a superplasticizer with higher cement contents (500-730 Kg/M³) was studied by Brooks and Wainwright (1979) in the University of Leeds, U.K. Their investigation compares strength, elasticity, shrinkage, swelling and creep of ultra-high strength concretes using naphthalene sulphonate superplasticizer and quartzizite coarse aggregate and sand (zone 3-4).

The following conclusions were drawn regarding the use of superplasticizer:

01. By using a superplasticising admixture with high cement contents (500-600 Kg/M³) to produce mixes of normal consistency, 28 day cube strengths of approximately 90 N/Sq.mm can be achieved. Compared with control mixes having the same cement content and consistency, the 28 day cube strength represents an increase of 19%. The higher strength of the admixture concretes is achieved by a reduction in water/cement ratio, the influence of which is more pronounced at early ages but less effective at later ages. Similar patterns of behaviour occur for both wet and dry stored concrete.
02. Compared with plain control concretes, the admixture concretes have correspondingly higher indirect tensile strength and moduli of elasticity. The established relations between tensile strength and cube strength and between modulus of elasticity and cube strength for control concrete are also applicable to the admixture concretes.

03. After one year of storage in water, the swelling of admixture concrete was approximately 50% greater than that of the control plain concrete. Since swelling of plain concrete increases with an increase in cement content, it can be postulated that the higher swelling of the admixture concrete is due to a higher hydrated cement paste content because of a rapid early-age strength development. An alternative explanation is that the admixture modifies the paste structure so that its swelling capacity increases.

04. Shrinkage of very high cement-content mixes does not conform with that anticipated. This is possibly because of microcracking which does not contribute to measured shrinkage strain. Shrinkage of an admixture concrete is less than the control concrete which again could be explained by the occurrence of more micro cracking in the case of admixture concrete, although there is no experimental corroboration of such a process.

05. Creep of high-cement content concrete stored in water cannot be assumed to be that of basic creep, since there is a swelling influence upon creep under drying conditions. In this investigation, the general level of creep under saturated conditions was observed to be equal to creep under drying conditions. As a result of the swelling influence, the creep of
admixture concrete is larger than creep of respective control concretes.

06. The general trend of creep, under drying conditions, does not follow that of shrinkage. It could be postulated that this trend is due to microcracking which, in contrast to shrinkage, does contribute to measured creep strain. Creep of the admixture concretes is similar to control concrete for 500 Kg/M³ of cement, but greater for 600 Kg/M³ of cement.

An extensive study conducted on superplasticized concrete with high workability was reported by Dhir and Yap (1982) at University of Dundee, Department of Civil Engineering. The properties studied were flow characteristics, stability (bleeding and segregation) air content in the fresh state and compressive strength and drying shrinkage in the hardened state.

The study included the following:

1. Eight superplasticizers available in the U.K.

2. Dosage of superplasticizer from 0.5% to 3.5% by weight of cement in the mix.

3. Nominal design strengths of concrete at 28 days of 20, 40 and 60 N/mm².

4. Sand grading from lower to upper limits of zone 2 (BS 882).
A single ordinary portland cement was used throughout and irregular gravel was used as coarse aggregate. The following conclusions were drawn:

01. Superplasticizers, depending on their composition and concentration, have different fluidizing capability in relation to dosage, expressed as a percentage of cement content (by weight) of the mix. A ranking order for the superplasticizer was given. This order is not affected by the cement content of the mix or by the fineness of sand within zone 2, and highlights the better performance of the category B superplasticizers.

02. Variations in cement content and sand fineness can affect the dosage requirements for flowing concrete. No single 'ideal' dose is available to cover all site conditions. Therefore it is strongly recommended that trial mixes should be used in order to ascertain the optimum dosage. It is proposed that the behaviour of flowing concrete in response to the above variations should be considered during the concrete production stage.

03. No definite relationship can be found for the initial and final flow table spreads. Where fully flowing concrete is not required, superplasticiser can be used at a certain 'optimum' dosage to produce a concrete which can have maximum workability with a minimum energy input.

04. It is proposed that segregation can be controlled by increasing the fineness of sand in preference to the cement content.

05. The bleeding of superplasticized concrete is higher than that of normal concrete and increases, although not linearly, with the dosage used. It also varies with different superplasticizers and sand gradings, but can be decreased by increasing the cement
content or fineness of sand of the mix. It is suggested that this susceptibility for higher bleeding should be borne in mind at the design stage, particularly with deep structures.

06. The air content of a mix is generally decreased by the addition of superplasticizer. The air content also increases with fineness of sand but decreases with an increase in cement content.

07. In general, the difference in the strength values of mixes incorporating different dosages of the same superplasticizer, for a given age, sand grading, curing environment and strength level, is small. Therefore no clear trend can be found for the effect of increase in dosage.

08. Upto 24 hours, the superplasticized concrete exhibits varying degrees of reduction in strength development when compared with the corresponding strength of normal concrete. This difference in strength between the two types of concrete is, however, small and, in practice, can be ignored.

09. The strength development, between 3 and 90 days, of superplasticized concrete is generally of the same order as that of normal concrete.

10. The drying shrinkage of superplasticized concrete is higher than that for normal concrete and increases with the superplasticizer dosage. At constant cement and aggregate contents, increasing the sand fineness increases the shrinkage; a similar trend was found for increasing the cement content of the mixes. For flowing concrete at a flow of 51 cm, the increase in shrinkage was between 5 and 25%, and at a flow of 62 cm between 7 and 27%, as much as that of the normal concrete. The use of
low-shrinkage aggregates is recommended in the production of flowing concrete to offset the increased shrinkage potential of this concrete.

The durability properties of superplasticized flowing concrete was investigated by Dhir and Yap (1983) at the University of Dundee, U.K. The following two aspects of durability response of strictly flowing concrete were studied: namely, (i) its resistance to freezing and thawing and (ii) wetting and drying.

It was found that the resistance to freezing and thawing of normally cured flowing concrete with up to 471 Kg/M³ cement content was found to be significantly inferior to that of normal concrete. Under repeated wetting and drying, flowing concrete specimen were found to be less durable than the corresponding normal concrete.

The properties of high strength concrete with silica fume using high range water reducer of the slump retaining type was investigated by Mitsmi, Kasami et al., (1989) at the technical research laboratory, Takenaka corporation, Tokyo, Japan. Here the mix proportions and admixture dosage variations on the rheological and mechanical properties of concrete before and after hardening were examined. The new superplasticizers showed good slump retention capabilities. Therefore its performance was much better than superplasticizers based on sulphonated naphthalene formaldehyde condensate, which lose their effectiveness at higher temperatures.

A study to optimise the type and dosage of superplasticizers in fly ash and silica fume concretes was conducted by Collepardi, Monosi et al., (1989) at the University of Ancona, Italy. In this study, two types of superplasticizers based on high range water reducers based on sulphonated naphtalene polymer (SNP) and sulphonated melamine polymer (SMP) - both as 40% aqueous solution have been used in the presence of fly ash or silica.
fume to manufacture superplasticized flowing concrete containing ASTM Type I or Type III portland cements. The superplasticizer dosage and the pozzolan addition ranged from 2 to 4% and from 12 to 20% respectively by weight of cement. The cement content varied from 255 to 400 Kg/M³.

The results of the investigation indicate that only in the presence of ASTM Type III portland cement, superplasticized fly ash concrete can be as strong as the corresponding silica fume concrete, particularly at relatively high cement factors (≥ 300 Kg/M³).

Swamy (1989) in his paper on ‘Superplasticizers and Concrete durability’, states that far too long water-reducing agents, plasticizers and superplasticizers have been looked upon as workability/pumping agents with possible savings in cement and increases in compressive strength. It is suggested that this concept is misleading and ill-informed. Whilst good workability is recognised as an essential component of placing and compacting, the more critical role of superplasticizers is to reduce the porosity of concrete through water reduction. The paper presents test data on concrete and mortar mixes with blended cements and superplasticizers and having water-binder ratios of 0.35 to 0.40. The properties of these concretes are presented and discussed in terms of strength development, permeability, pore structure, carbonation and micro structure. It is shown that superplasticizers should be seen as agents of concrete durability rather than as agents of concrete workability.

Samarai et al., (1989) have studied the effects of retempering with superplasticizer on properties of fresh and hardened concrete mixed at high ambient temperatures. A total of 15 concrete mixes with water-cement ratios 0.40, 0.50 and 0.60 were made at ambient temperatures 30, 40, 50, 55 and 60 degree centigrades to give a constant workability. Immediately after mixing and after two retemperings at 30 minute intervals, fresh concrete properties (slump, air content, concrete temperature and unit weight) were determined.
Specimens were cast after initial mixing and after two retemperings were tested for hardened concrete properties at 7 and 28 days.

The additional water and cement needed to achieve the same workability at higher temperatures is very high for low W/C concrete, whereas there is only a slight increase in the water demand for concretes with W/C 0.50 and 0.60. The increase in the rate of slump loss is not significantly higher at higher temperatures. When retempering with superplasticizer, there are no detrimental effects on fresh as well as hardened concrete properties even under the unfavorable high ambient temperature of 60 degree centigrade. The performance characteristics are the same for concretes mixed at higher ambient temperatures and retempered with superplasticizer.

With increase in trend towards the wider use of concrete for prestressed concrete in bridges and high-rise buildings, there is a growing demand for concrete of higher compressive strength than has been hitherto adopted.

In India, over the past decade several manufacturers have brought out a range of admixtures for use in concrete. This, coupled with availability of grade 43 and 53 cements have made possible the production of high strength concretes.

1.9 SCOPE OF WORK

The following is the scope of work:

01. To establish the water-cement ratio compressive strength relationship for superplasticized concrete with grade 43 and grade 53 cements, for category A and B superplasticizers, for crushed granite aggregates.
02. To study the adsorption characteristics of various grades of cements on high early strength type superplasticizers.

03. To study the dispersing capability of high early strength superplasticizers on various grades of cements.

04. To study the compatibility of superplasticizers with grade 43 and grade 53 cements - especially the problems associated with slump retention.

05. To study the effect of temperature on the compatibility of superplasticizers.