STUDY OF CEMENT-SUPERPLASTICIZER INTERACTION AND ITS IMPLICATIONS FOR CONCRETE PERFORMANCE

A THESIS

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THESIS CERTIFICATE

This is to certify that the thesis entitled “**STUDY OF CEMENT-SUPERPLASTICIZER INTERACTION AND ITS IMPLICATIONS FOR CONCRETE PERFORMANCE”** submitted by **C. Jayasree** to the Indian Institute of Technology Madras for the award of the degree of **Doctor of Philosophy** is a bonafide record of research work carried out by her under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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ABSTRACT

Chemical admixtures, particularly superplasticizers have become indispensable because of their beneficial effects in fresh and hardened concrete. However, the compatibility between the cement and admixture, which is influenced by the characteristics of cement paste, and the type and dosage of admixtures, could affect the benefits of incorporating a superplasticizer. It is, therefore, essential to understand the mechanisms that influence the cement-superplasticizer interaction for selecting an appropriate type of admixture at an optimum dosage. The current study addresses these and other specific issues pertaining to the performance of concrete incorporating chemical and mineral admixtures, especially superplasticizers.

A suitable mixing method for the preparation of paste is first selected so that the paste prepared will be representative of that of concrete. In order to evaluate the influence of superplasticizers and cement characteristics, studies are conducted with four families of superplasticizers and four types of cements on fluidity, loss of fluidity and setting behaviour. The relative fluidity of different superplasticized pastes are studied with the Marsh cone, mini-slump and viscometric tests for evaluating the best combination. The Marsh cone flow time, yield stress and plastic viscosity decreases whereas the mini-slump spread increases with an increase in the dosage of the superplasticizer upto the saturation dosage, after which they remain constant. An experimental and analytical validation of the Marsh cone test is done using rheological models to understand its effectiveness in capturing the relative fluidity.

The correlation between the flow behaviour of paste with normal concrete and self compacting concrete shows that the saturation dosages obtained from paste and mortar are comparable whereas a dosage slightly higher than the saturation dosage of the paste is required for adequate workability in concrete. The setting behaviour is studied through Vicat penetration and electrical conductivity methods. Both tests confirm that superplasticizers retard the setting of cement paste; however, the extent of retardation varies with the type of superplasticizer.

Another aspect studied in this work is the influence of the superplasticizer on the hydration processes and on the development of microstructure of hydrated cement paste. With this aim, cement pastes are analyzed using several characterization techniques (X-ray diffraction, scanning electron microscopy, thermal analysis and Si nuclear magnetic resonance). The test results clearly indicate the influence of superplasticizers in delaying the hydration. The superplasticizer delays the formation of ettringite as well as the silicate polymerization; however, it produces a dense and uniform microstructure, enhancing the strength development.

The absorbance study using a UV spectrometer gives insight into the influence of cement and superplasticizer characteristics on the absorbance of the superplasticizers and its variation with time. The study of the influence of other admixtures on the cement-superplasticizer interaction shows that the addition of metakaolin and viscosity modifying admixtures increases the saturation dosage of the superplasticizer and the viscosity of the paste.

Finally, based on the test results, a simple methodology is recommended to select a compatible cement-superplasticizer combination is recommended. The use of Marsh cone and Vicat penetration tests in the paste phase, and final trials on concrete for strength and cost evaluation are suggested as part of this methodology.

Keywords: Superplasticizer; Marsh cone; mini-slump; rheology; loss of fluidity; compatibility.

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

Recent advances in concrete technology have generally resulted in better performance of concrete in terms of strength, workability and durability over the past few decades. The enhancement of fresh and hardened state properties has been achieved especially through the incorporation of chemical and mineral admixtures. The multifunctional benefits of chemical admixtures, such as the high range water reducers (HRWRs) or superplasticizers, have made them essential components of modern high quality concrete. Today's high performance concretes require superplasticizers in order to reduce the water content while maintaining high workability, so that better mechanical integrity and lower permeability are obtained when compared to conventional concretes.

Though the primary purpose of adding superplasticizers is to provide high workability, their incorporation in concrete could also affect, sometimes negatively, the hardening and hardened state properties (Ramachandran, 2002; Mailvaganam, 2001). Moreover, phenomena such as loss in the workability of concrete, rapid/slow setting, air entrainment, excessive bleeding and segregation could result from the improper use of superplasticizers. Therefore, a good understanding of the cement-superplasticizer interaction is required for better utilization of high performance concrete, and for the further improvement of the properties of the superplasticizers and concrete.

The performance of a superplasticizer in concrete depends on its properties, as well as that of the cement, in addition to the concrete mix proportions and environmental conditions (Jolicoeur and Simard, 1998). The major characteristics of cement that could affect the performance of chemical admixtures are the C_3A/SO_3 ratio, alkali content and nature of sulphates whereas the chemical structure and molecular weight of polymers are the principal characteristics of superplasticizers (Rixom and Mailvaganam, 1999; Ramachandran, 2002). The main action of the superplasticizers is electrostatic repulsion and steric hindrance that result in the dispersion of the cement particles (Ramachandran et al., 1998). Nevertheless, the four different families - lignosulphonates, melamines, naphthalenes and polycarboxylates - each has different distinguishing characteristics and effects (Rixom and Mailvaganam, 1999).

The proposed study focuses on the improvement of the flow behaviour and its characterization, and the understanding of the microstructure of the superplasticized cement-based materials. More specifically, the optimization of the superplasticizer dosage, determination of the rheological behaviour, setting and evolution of the hydration products are evaluated from tests of cement paste. The study also addresses the issues of loss of workability and set retardation, which could arise as a result of cement-superplasticizer incompatibility.

The relevance of the present work in the Indian context can be appreciated by considering the following points. The types and number of superplasticizers available in the market have increased significantly over the past few years. The usage of products without adequate knowledge of their effects, along with the use of high superplasticizer dosages, has led to significant problems during construction, some of which can be attributed to cement-admixture incompatibility. The current knowledge of materials and practices involved in the use of superplasticized concrete is mostly based on foreign experience, which is not always directly applicable to construction in India today. For example, the tendency to use synthetic gypsum instead of natural gypsum during cement production results in the increase of superplasticizer dosage and setting time. Also, ready-mix concrete in most construction sites is expected to be placeable even 3-5 hours after mixing.

The final aim of the work is to identify the factors that affect the cement-superplasticizer interaction and to propose remedial measures for the concrete user to avoid incompatibilities through a materials science approach. Commercially-available superplasticizers of different types, several cements, mineral admixtures and viscosity modifying admixtures are used in the study in order to span the wide spectrum of products used in the manufacture of high performance concrete.

1.2 OBJECTIVES AND SCOPE

The present thesis focuses on the study of the mechanisms that affect the cement-superplasticizer interaction, which in turn influence the fresh and hardened state properties of the cement based material. The main objectives of the research are:

- To identify a suitable mixing method for the preparation of pastes such that it will represent the paste phase of concrete.
- To evaluate the flow behaviour of superplasticized cement paste using simple methods, and correlating it with rheological characteristics for validating the use of simple test methods.
- To analyze the correlation between the fluidity of cement paste, mortar and concrete, in order to validate the optimization of the cement paste composition as the first step in the mix design of high performance concrete.
- To study the influence of superplasticizer on the hydration processes and on the microstructural development of cement paste.

- To identify the characteristics of cement and superplasticizer that can affect the behaviour of the cement-superplasticizer system and propose guidelines to avoid incompatibilities.

The scope of the study is limited to the following with respect to main components and methods adopted:

- Four types of cements available in India and products from four families of superplasticizers.
- Empirical correlation between the behaviour of cement paste and concrete is made through experimental studies.

1.3 STRUCTURE OF THE THESIS

The research strategy that was followed in order to achieve the objectives specified in the previous section and the results obtained are described in the following chapters of the thesis.

A detailed review of the influence of superplasticizers on the hydration of cement is given in Chapter 2, along with appropriate comparisons with the hydration of pure cement. The characteristics, chemistry and mechanisms of action of superplasticizers are also presented. The factors affecting the cement-superplasticizer interaction, mainly, the chemical structure of the superplasticizer and the cement characteristics are reviewed, and the need and motivation for conducting this study are emphasized in the same Chapter.

Chapter 3 begins with the selection of a suitable procedure for the preparation of superplasticized cement paste that simulates the paste phase of concrete. The determination of the saturation dosage of superplasticizer with the Marsh cone is explained in detail. The influence of the type and dosage of superplasticizer on the flow behaviour of paste is evaluated through the Marsh cone, mini-slump and viscometer tests. In order to validate the use of simple engineering-level test methods, the Marsh cone flow time and mini-slump spread are shown to correlate well with rheological parameters through appropriate analytical models. This chapter also analyses the influence of saturation dosage of superplasticizer on the loss of fluidity of different cement-superplasticizer combinations. Appendix A contains the results for establishing the correlation between simple tests with rheological parameters. The matlab programme for predicting the Marsh cone flow time using rheological model is presented in Appendix B. The viscoelastic characterization of pure cement paste and superplasticized cement paste, using creep and recovery and stress relaxation tests, is given in Appendix C. The influence of type and dosage of superplasticizers on the change in rheological response, from viscoelastic to viscous nature, is also explained.

Chapter 4 deals with the correlation between the flow behaviour of superplasticized cement paste, mortar and concrete. The setting behaviour of paste and the set retardation due to the use of superplasticizers are studied with the Vicat apparatus and electrical conductivity measurements. The responses of paste, mortar and concrete in terms of loss of fluidity and setting are compared using appropriate tests. The influence of superplasticizer dosage on the compressive strength of concrete and its evolution with age has also been studied.

The study of the effect of the superplasticizer on the hydration processes, as well as on the microstructural development, through several complementary physico-chemical characterization techniques like X-ray diffraction, scanning electron microscopy, thermal methods and nuclear magnetic resonance is presented in Chapter 5. It is intended to provide an overall picture of the influence of different families of superplasticizers on the types of hydrated products as well as their rate and amount of formation.

Chapter 6 presents the evaluation of the compatibility between different cements and superplasticizers through flow and setting tests. The variations of the dosages and loss of fluidity for different superplasticizers is explained based on an absorbance study using a UV spectrophotometer. Subsequently, a methodology based on the test results, for selecting a compatible combination of cement and superplasticizer is recommended. The studied combinations are evaluated with the recommended methodology and finally the same is validated with other approaches for selecting the compatible combination.

Chapter 7 deals with the influence of mineral admixtures and viscosity modifying admixtures on the cement-superplasticizer interactions. A mix design procedure for self compacting concrete incorporating VMA is suggested in line with previous studies. The validation of the use of the saturation superplasticizer dosage obtained from tests on pastes is illustrated with the characterization of self compacting concrete through the slump flow, V-Funnel and J-Ring tests.

The conclusions drawn from the research work are summarized and the guidelines for selecting the superplasticizers are presented in Chapter 8. Also, the scope for further research is highlighted.

CHAPTER 2

STATE-OF THE-ART REPORT ON CEMENT-SUPERPLASTICIZER INTERACTION

2.1 GENERAL

Admixtures, both mineral and chemical, have become essential components of high quality concrete and are added to concrete at the mixing stage to modify its properties in the fresh and hardened state. ACI 116R (2000) defines the admixture as ‘a material other than water, aggregates, hydraulic cement and fiber reinforcement, used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing’. Common mineral admixtures are silica fume, fly ash, ground granulated blast furnace slag and metakaolin, the incorporation of which can improve strength, as well the durability of the concrete. The incorporation of chemical admixtures can vary significantly with the application; e.g., air entraining admixtures are very common in colder regions where the concrete is prone to freeze-thaw damage, set accelerators are essential in wet-mix shotcreting, and retarders are common when the ready-mix concrete has to be transported over long distances. However, the superplasticizer or water reducer is an admixture that has become an important component of all high quality concretes; the addition of the superplasticizer improves the workability at low water content, and consequently leading to good fluidity in the fresh state, reduction in concrete porosity and compositional stability when the concrete is being transported and placed. The use of superplasticizers/high range water reducers in concrete has played a central role in the development of high strength and high performance concretes, without which such concretes would not be technically feasible.

However, the performance of an admixture in concrete is dependent on many factors, like the nature and amount of admixture, nature of cement and aggregates, water-cement ratio and environmental conditions. In addition, some problems could commonly arise as a result of the incompatibility between cement and water reducers, such as rapid loss of workability, rapid/retardation of setting and low rates of strength gain. Sometimes, the incompatibility could even occur between a particular admixture and only some batches of the same brand of cement (probably made at different plants), suggesting that the problem is complex from the user's point of view. Therefore, the understanding of the effects of superplasticizers on the properties of concrete is essential for further improvement of the properties and behaviour of both the superplasticizer and concrete.

The objective of this chapter is to summarise the various factors responsible for the physico-chemical reactions in order to have a better understanding of cement-superplasticizer interaction. Some relevant aspects of cement composition and cement hydration reactions are also described in order to understand the action of the superplasticizer in a cementitious system. A detailed review of the different families of superplasticizers, mechanisms of action and their characteristics that could control their compatibility with cement is also given.

2.2 CEMENT CHEMISTRY

2.2.1 Raw Materials Used in Cement Manufacture

The raw materials used for the production of cement include calcareous materials and argillaceous materials. CaO is obtained from limestone, principally calcite; the lime can be either quick lime, dolomite lime or magnesium lime. In quick lime, the major part is CaO or MgO. Dolomite lime indicates that there is 35-45% magnesium carbonate while the magnesium lime indicates the presence of 5-35% of magnesium carbonate in the limestone. Silica (SiO_2) exists naturally in the fine state as different crystalline polymorphs (e.g., α-quartz, cristobalite, tridymite) and as impure poorly crystallized or amorphous minerals (e.g., opal and flint). It is introduced through the aluminosilicate minerals of the shale or clay component of kiln feed and combine with CaO during clinkering process to form the impure calcium silicates, alite and belite. The other two significant oxides, namely aluminium oxide that occurs in nature as α-Al_2O_3 (Corundum) and iron oxide are derived from clay and shale (Hewlett, 2004).

Gypsum and anhydrite (i.e., anhydrous calcium sulphate) are found naturally in many parts of the World; in Asia, India has the largest reserves of natural gypsum, 95% of which is found in Rajasthan (Shah, 2006). Natural gypsum used for cement production in India could be from marine or desert sources. Calcium sulphate is also available as a byproduct of the acid based manufacture of fertilizers from phosphate ore. However, when this is used in cement production, it causes an increase in setting time due to the presence of water soluble fluorine, water soluble phosphates and phosphates in the crystal lattice of gypsum (Hewlett, 2004). Nevertheless, such synthetic gypsum of good quality is readily available and, consequently, there is a growing in tendency to use it instead of natural gypsum in the Indian cement manufacturing industry.

2.2.2 Cement Composition

Portland cements are multicomponent multiphase inorganic materials and consist of five major constituents in varying amounts. In the early ages of a cement-based material, the two calcium silicates – tricalcium silicate (C_3S) and dicalcium silicate (C_2S) control the strength and its evolution, and the two aluminates - tricalcium aluminate (C_3A) and tetra calcium alumino ferrite (C_4AF) and the sulphate phases (i.e., gypsum) influence the setting behaviour (Hewlett, 2004). In addition to these main compounds, there are minor compounds, such as MgO, TiO_2, Mn_2O_3, K_2O and Na_2O. Two of the minor compounds, i.e., sodium and potassium oxides, known as alkalis, play an important role in the cementitious system in terms of the rheological behaviour, and cement-superplasticizer interactions.

Standards such as those of ASTM, BIS and CEN give the acceptable ranges of components for different classes of cements. For example, the ASTM C 150 (2007) standard, limits the tricalcium silicates to 35%, tricalcium aluminates to 7%, and tetra calcium alumina ferrite to 25%, and specifies a minimum dicalcium silicate content of 40%, along with a maximum alkali content of 0.6% $(Na_2O)_{eq}$ (Hewlett, 2004); a typical cement corresponding to this standard could have the composition as shown in Table 2.1.

Table 2.1 Typical portland cement composition
conforming to ASTM C 150

Type of compound	Composition (%)
C_3S and C_2S	70-80
C_3A	0-16
C_4AF	1-17
MgO	0.5 -6
Na_2SO_4, K_2SO_4	0.5-3
Free lime	0.2-4
Gypsum	4
Low alkali cement	< 0.6 $(Na_2O)_{eq}$

The chemical and physical requirements of different grades of cement as per the IS codes are given in Table 2.2. It should be noted that the IS codes do not specify the limits for alkalis (as done by ASTM C 150 (2007))which lead to significantly different rheological behaviour especially if the alkali content varies considerably. Similarly, the code does not prescribe upper limits of the alumina ratio and specific surface area, both of which can affect the performance of the cement in the fresh and setting stages. It can be seen from the table that the only differences between the different grades of cement are in the rate of compressive strength gain and the 28-day value.

Table 2.2 Requirements of different grades of cement as per IS codes.

Characteristics	Requirements		
	33 grade (as per IS 269-1989)	43 grade (as per IS 8112-1989)	53 grade (as per IS 12269-1987)
Lime saturation factor *	Not greater than 1.02 and not less than 0.66	Not greater than 1.02 and not less than 0.66	Not greater than 1.02 and not less than 0.8
Alumina ratio**	Not less than 0.66	Not less than 0.66	Not less than 0.66
Insoluble residue by mass	Not more than 4%	Not more than 2%	Not more than 2%
Magnesia, % by mass	Not more than 6%	Not more than 6%	Not more than 6%
Total sulphur content calculated as sulphuric anhydride (SO_3), % by mass	Not more than 2.5 and 3.0 when C_3A % by mass is 5 or less and greater than 5, respectively	Not more than 2.5 and 3.0 when C_3A % by mass is 5 or less and greater than 5, respectively	Not more than 2.5 and 3.0 when C_3A % by mass is 5 or less and greater than 5, respectively
Total loss on ignition	Not more than 5%	Not more than 5%	Not more than 4%
Fineness	Specific surface shall not be less than 225 m^2/kg	Specific surface shall not be less than 225 m^2/kg	Specific surface shall not be less than 225 m^2/kg
Initial setting time	Not less than 30 minutes	Not less than 30 minutes	Not less than 30 minutes
Final setting time	Not more than 600 minutes	Not more than 600 minutes	Not more than 600 minutes
Compressive strength	For, 72 ± 1h, not less than 16 MPa For, 168 ± 2h, not less than 22 MPa For, 672 ± 4h, not less than 33 MPa	For, 72 ± 1h, not less than 23 MPa For, 168 ± 2h, not less than 33 MPa For, 672 ± 4h, not less than 43 MPa	For, 72 ± 1h, not less than 27 MPa For, 168 ± 2h, not less than 37 MPa For, 672 ± 4h, not less than 53 MPa

*Lime saturation factor = Ratio of percentage of lime to percentage of silica, alumina and iron oxide represented as $(CaO - 0.7\ SO_3)/(2.8\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3)$.

**Alumina ratio = Ratio of percentage of alumina to iron oxide.

Though cements are classified by national or international standards, as seen earlier, the chemical composition of a type of cement can vary within certain limits between brands and even batches, depending on the raw materials and production processes. For example, in Table 2.3 (from Hewlett, 2004), which gives the chemical analyses of six different CEM I portland cements available in the UK in 1987, it can be seen that the compound composition, fineness and particle size distribution vary significantly from one cement to another, though they all belong to the same "standard" type. Consequently, different cements of the same type/grade can have significantly different characteristics that can lead to differences in the interactions between the cement and admixture.

Table 2.3 Chemical analyses of some CEM I portland cements of UK (Hewlett, 2004)

Type of compound (%)	DO	DOX	EO	FO	GO	HO
$Si\,O_2$	22.2	21.8	20.9	20.1	19.5	20.2
$Al_2\,O_3$	4.2	4.1	4.6	5.0	6.2	5.3
$Fe_2\,O_3$	2.4	3.3	2.1	2.8	2.0	2.2
$Mn_2\,O_3$	0.08	0.07	0.06	0.16	0.03	0.04
$P_2\,O_5$	0.15	0.1	0.23	0.1	0.17	0.07
$Ti\,O_2$	0.27	0.23	0.2	0.2	0.31	0.23
Ca O	63.9	64.2	66.3	63.2	64.7	66.4
Mg O	1.0	1.4	0.8	2.2	1.2	0.9
SO_3	2.7	2.5	2.8	3.0	3.0	2.5
CO_2	0.79	0.3	0.48	-----	----	----
$K_2\,O$	0.74	0.61	0.8	0.78	0.43	0.56
$Na_2\,O$	0.14	0.15	0.16	0.13	0.24	0.23
Free lime	1.5	1.4	1.4	2.1	0.9	1.2
Loss on ignition	1.7	1.5	0.75	1.0	1.1	0.7
Insoluble residue	1.7	0.8	1.1	0.84	0.85	0.5
Na_2O equivalent	0.63	0.55	0.69	0.64	0.52	0.6
$C_3\,S$	46	51	63	50	58	66
$C_2\,S$	29	24	12	20	12	8
$C_3\,A$	7.1	5.3	8.6	8.5	13	10.3
C_4AF	7.3	10	6.4	8.5	6.1	6.7
Density(kg/m^3)	3130	3130	-	3150	3110	3140
Surface area (m^2/kg)	383	380	-	443	394	344
Particles coarser than 45μm	13.4	12.5	-	9.0	12.3	17.4

2.2.3 Hydration of Cement

2.2.3.1 Hydration of Cement Compounds

Hydration of cement is the key to concrete performance in terms of setting, durability and strength. It includes the hydration of calcium silicates, calcium aluminates and calcium aluminoferrite. When water is added to cement, each of the compounds undergoes reactions but with different characteristic contributions to the setting, strength gain and other properties of the hardened cement paste; e.g., tricalcium silicate hydration affects the early age response while the hydration of dicalcium silicate affects the strength at later ages. The relevant aspects of the hydration of the various components of cement are explained in the following paragraphs. It should be noted that, by volume, calcium silicate hydrate (C-S-H) constitutes 60-70% of the hydration products, calcium hydroxide constitutes 20-25% and 5-15% is made up of other minor phases.

Upon the addition of water, tricalcium silicate (C_3S) rapidly reacts to release calcium ions, hydroxide ions and a large amount of heat. The pH quickly raises to over 12 because of reaction alkaline hydroxide (OH^-) ions. This initial hydrolysis slows down quickly resulting in a decrease in the heat evolved. The reaction continues slowly, producing calcium and hydroxide ions until the system saturates. Once this occurs, $Ca(OH)_2$ starts to crystallize. Simultaneously, calcium silicate hydrate begins to form. Subsequently, calcium and hydroxide ions precipitate out of solution accelerating the hydration of tricalcium silicate. The C-S-H crystals grow thicker making it more difficult for water molecules to reach the unhydrated tricalcium silicate. Consequently, the speed of reaction is controlled by the rate at which water molecules diffuse through the C-S-H coating on the surface of the unhydrated cement particles. As the coating thickness increases, the production of C-S-H becomes slower and slower (Jolicoeur and Simard, 1998). The overall chemical reaction and the heat evolved (ΔH) are given in the following equation:

$2C_3S+6H \Rightarrow C_3S_2H_3+ 3\ CH\ (\Delta H = -520\ kJ/kg)$ (2.1)

Dicalcium silicate reacts with water in a similar manner as C_3S but much more slowly, according to the reaction and heat of hydration shown below:

$2C_2S+4H \Rightarrow C_3S_2H_3+ CH\ (\Delta H = -260\ kJ/kg)$ (2.2)

The hydration of tricalcium aluminate (C_3A) in the presence of gypsum occurs as follows:

$2\ C_3A+ H+ CS \Rightarrow C_6AS_3\ H_{32}+ 3CH\ (\Delta H = -910\ kJ/kg)$ (2.3)

Calcium aluminate hydrate or ettringite (AFt) needles cover the surface of hydrating calcium aluminate particle and prevent further hydration. If the supply of sulphate from gypsum is exhausted before C_3A is completely hydrated, a second reaction can occur resulting in the formation of calcium monosulphoaluminate (AFm). This reaction may occur before the formation of the ettringite if the availability of gypsum is lower than that required by the rate of reaction of C_3A and sulphate ions. If monosulphoaluminate is exposed subsequently to sulphate ions, new reactions will occur leading to the formation of more ettringite.

Calcium aluminoferrite forms the same hydration products as C_3A, with a slow rate of reaction that is decreased further by gypsum and higher iron oxide content. The reaction is as given by the following equation:

$C_4AF + CS\ H_2 +12H \Rightarrow C_4\,(A,F)\ CSH_{12}\ \ (\Delta H = -420\ kJ/kg)$ (2.4)

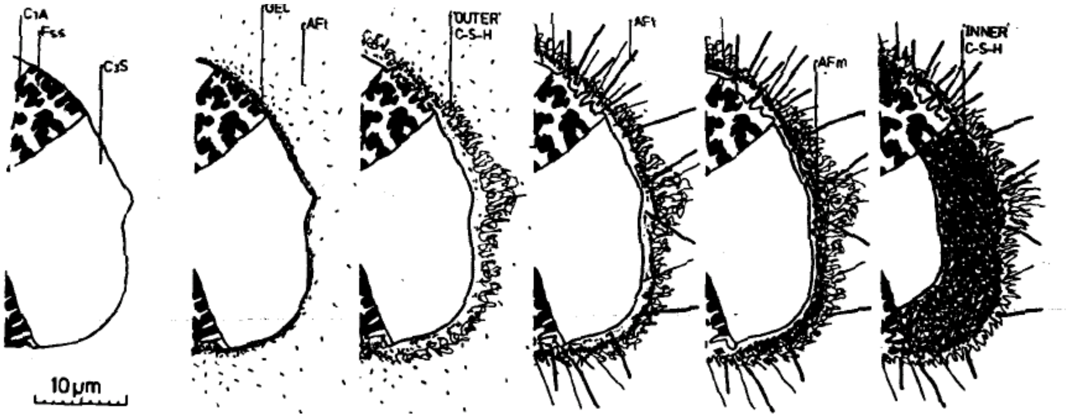
The relative reactivity of different mineral phases with water can be given as $C_3A >$ $C_3S > C_2S > C_4AF$; accordingly, the aluminate phases and their hydration products play an important role in the early hydration processes and cement-admixture interactions.

2.2.3.2 Hydration of the Portland Cement Grain

The development of the microstructure of a typical polymineralic cement grain is shown in Figure 2.1, and the major unhydrated compounds present are shown in Figure 2.1 (a). After the first contact of cement with water, various reactions occur that result in a typical heat evolution pattern with time, through which four stages can be identified in the early hydration process: initial hydration period, dormant period, acceleration and deceleration period. The basic mechanisms mostly influenced by the presence of admixtures, particularly those occurring in the early hydration processes are described below (Mehta and Monteiro, 2005; Jolicoeur and Simard, 1998; Taylor, 1997; Neville, 2000; Hewlett, 2004):

Initial hydration (0-15 minutes): During this period, rapid heat generation, called as heat of wetting, occurs on mixing cement with water. Easily soluble components like alkalis, calcium, sulphate phases and free lime are dissolved in the surrounding water and the solubilization of variety of ionic species like Na^+, K^+, Ca^{2+}, SO_4^{2-}, and OH^- ions takes place. Hence, the wetting of cement particles and subsequent dissolution of ions lead to the formation of an amorphous gel layer over the surface of grains. Beyond the solubilization process, the formation of solid hydration product is governed by the nucleation process. The initial nucleation process involves the formation of calcium sulphoaluminate or ettringite from Ca^{2+}, $SO_4^{2-}$and $Al(OH)_4^-$ ions on the outer surface of layer of gel, as shown in Figure 2.1 (b). This reaction is the most important as far as the rheology of the fresh cement paste is concerned. The initial C_3A dissolution may be increased by the presence of more dissolved alkalis (Spiratos et al., 2003). After some time, the cement grains are coated with a protective layer of hydration products. At this stage, the rate of reactions sharply reduces resulting in less heat of hydration.

The presence of organic admixtures can interfere with these nucleation and growth processes resulting in the change of the hydration reactions and hydration products. Also, after the first few minutes, the chemical admixtures interact with these hydration products instead of hydrating compounds.



(a) (b) (c) (d) (e) (f)

Fig. 2.1 Microstructure of hydrated portland cement (Taylor, 1997)

Dormant period (2-4 hours): During this period, the mix remains plastic and very low heat generation takes place, indicating that all the reactions are slow. This is due to two reasons: (1) the gel formed in the first stage acts as a diffusion barrier around the C_3S; (2) the SiO_2 rich electrical double layer formed around C_3S and the supersaturation of Ca^{2+}, OH^- and SO_4^{2-} in solution prevents further dissolution of ions. As the thickness increases, the time it takes for water to penetrate the coating increases; thus the reaction becomes diffusion controlled.

In the presence of an adequate concentration of SO_4^{2-} ions, continued growth of ettringite crystals takes place. Simultaneously, the reaction of C_3S produces 'outer product' C-S-H on the AFt, leaving space between the grain and hydrated shell, as shown in Figure 2.1 (c). An inadequate concentration of SO_4^{2-} ions leads to the formation of calcium aluminate hydrate (C-A-H) resulting in flash set. If the SO_4^{2-} concentration is too high due to the presence of hemihydrates and alkali sulphates, massive nucleation and growth of gypsum crystals (false set) occurs.

The interaction of a chemical admixture with any of these reactions or reactive species significantly affects the behaviour of cement pastes and concretes during the induction period.

Acceleration period (4-8 hrs): Several theories have been put forward to explain the end of the dormant period or the start of the acceleration period: Weakening of the double layer by further hydration, increased diffusion and weakening of ionic strength around the hydrating particle all result in the end of the dormant period and the beginning of a new stage of high chemical activity, called the acceleration period. However, during this period, the suspension loses its plasticity and is converted to a stiffer matrix, which is no longer fluid. Subsequently, the secondary hydration of C_3A produces long rods of AFt and the intense hydration of C_3S during the acceleration period results in the formation of 'inner product' C-S-H and precipitation of C-H, as shown in Figure 2.1 (d). Later, C_2S starts to hydrate and, to a lesser extent, C_4AF continues to hydrate. During the acceleration period, the calcium and sulphate ion concentrations in the pore water decrease due to the ettringite formation.

The chemical admixtures may influence the formation and properties of the protective hydrate layer in the acceleration stage. Also, the admixtures remaining in the aqueous solution further influence the nucleation and growth of the hydration products.

Deceleration period (8-24 hours): The reactions are slow and completely diffusion dependent in this period, which is reflected by the hardening of the cement paste. Due to the depletion of sulphate ions in the pore water, C_3A reacts with the AFt forming hexagonal plates of monosulphate (AFm), as shown in Figure 2.1 (e). The pore volume decreases with increasing time and decreasing free water content as hydration progresses with the formation of C-S-H gel and C-H. This is followed by a steady state (12-24 hours) in which temperature has little influence on hydration.

Later hydration results in the formation of sufficient ‘inner’ C-S-H to fill the space between grain and shell, as shown in Figure 2.1 (f). The outer C-S-H becomes more fibrous during this period and the ettringite is completely converted to monosulphoaluminate within 1 to 3 days.

2.3. WATER REDUCERS AND SUPERPLASTICIZERS

Water reducers are classified as normal, medium and high range depending on the level of water reduction possible due to its addition in concrete. Water reducers belong to the dispersant family; dispersants are long chain organic molecules having a polar hydrophilic end and non-polar hydrophobic groups that are adsorbed on the cement particles. Superplasticizers are high range water reducers and are incorporated in concrete either to maintain the same workability at reduced water cement ratio or to increase the workability by maintaining constant w/c. These admixtures are synthetic high molecular weight water-soluble polymers that are effective in dispersing the flocculated cement grains. Solubility is achieved by the presence of adequate hydroxyl, sulphonate or carboxylate groups attached to the main organic unit which is usually anionic (Rixom and Mailvaganam, 1999; Ramachandran, 2002; Bentur, 2002).

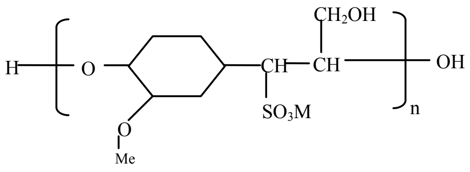
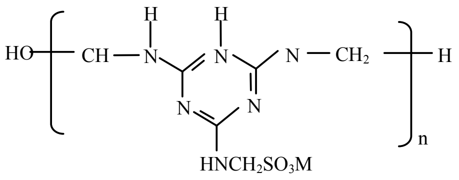
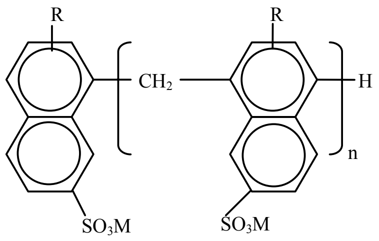
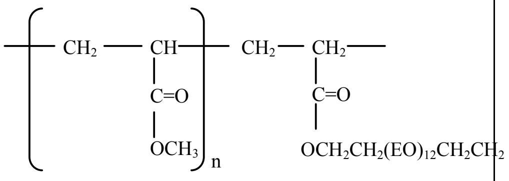
After the introduction of the first generation of superplasticizers in 1960s, these products have become essential for the placement of concrete in areas with low accessibility or with high density of reinforcement, as well as to provide an increase in the pumpability of concrete. In general, however, the reduction of w/c that can be obtained with the use of superplasticizers leads to higher strength and durability, making them common components of high performance and high quality concretes. Also, newly developed concretes such as self compacting concrete require the presence of a superplasticizer to achieve the desired properties.

2.3.1 Characteristics and Chemistry of Superplasticizers

Superplasticizers belong to four different families: modified lignosulphonates (LS), sulphonated naphthalene formaldehyde (SNF), sulphonated melamine formaldehyde condensates (SMF), and the new generation of superplasticizers, which is made up of copolymers that include polycarboxylates (PCE), polyphosphonates, polyacrylates and monovinyl alcohols (Rixom and Mailvaganam, 1999; Ramachandran, 2002). The different families of superplasticizers are generally based on chemicals of the type presented in Table 2.4.

The lignosulphonate based admixtures are normal water reducers and at higher dosages of such admixtures, excessive retardation of set and entrainment of air occurs, which limits their dosage in practice (Ramachandran, 2002). Nevertheless, modified lignosulphonates, in which the sugar content is reduced, exhibit less retardation (Aïtcin, 1998). At higher molecular weights, they can be considered as superplasticizers and used for obtaining workable concrete, with some retardation of initial set (Ramachandran, 2002). It has also been found that sodium lignosulphonate is a better plasticizer than calcium lignosulphonate because the former has higher solubility.

Table 2.4 Chemical structure of superplasticizers (Rixom and Mailvaganam, 1999)

Class	Origin	Structure (typical repeated unit)
Lignosulphonates (LS)	Derived from neutralization, precipitation, and fermentation processes of the waste liquor obtained during production of paper-making pulp from wood	 Me =CH_3 , M =Na
Sulphonated melamine formaldehyde (SMF)	Manufactured by normal resinification of melamine - formaldehyde	 M = Na
Sulphonated naphthalene formaldehyde (SNF)	Produced from naphthalene by oleum or SO_3 sulphonation; subsequent reaction with formaldehyde leads to polymerization	 R =H,CH_3,
Polycarboxylic ether (PCE)	Free radical mechanism using peroxide initiators is used for polymerization process in these systems	 EO: Ethylene oxide

The first admixtures to be classified as superplasticizers were salts of SNF and SMF. All of these have the same functional groups, namely sulphonates. The use of SNF and SMF based superplasticizers resulted in significant water reduction at low dosages. The SNF based superplasticizers appear to yield the best fluidizing effect in the molecular weight range of 4000-40000 gm/mole, while at higher ranges the effect decreases (Ramachandran, 2002). SMF based superplasticizers generally have poorer slump retention characteristics, when compared with the SNF based products, and are, consequently, used more extensively in the pre-cast industry.

In the last few years, several polymeric surfactants with carboxyl, hydroxyl, and phosphonate functional groups have been introduced in the market as third generation superplasticizers, and are generically known as polycarboxylates. These are comb polymers and are characterized by long chains and side chains, in which the hydrophilic groups are in contact with water and hydrophobic groups are attached to cement particles (Tanaka et al., 1999; Sakai et al., 2003). The dispersion due to these superplasticizers depends on the length of the main chain, and the length and number of the side chains. In general, the polycarboxylates are sufficient in low dosages due to better dispersing action than first and second generation superplasticizers. Moreover, it appears that they can be tailored to fulfill the requirements of the application (Magarotto et al., 2003; Houst et al., 2005; Falikman et al., 2005). The mechanisms of action of superplasticizers are explained with more detail in the following section.

2.3.2 Mechanisms of Action of Superplasticizers

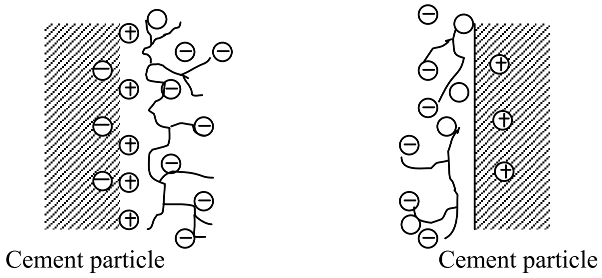
The rheology of cement paste is governed by van der Waal's attractive forces between the cement particles and the electrostatic repulsion due to the surface charges on the cement particles. However, as the former force is larger than the latter, cement particles tend to eventually flocculate. The action of the superplasticizer is to prevent or delay the flocculation and to disperse the cement particles within the paste. The different interactions between the cement and superplasticizer, which are often classified as physical or chemical interactions, are described in detail in the following paragraphs.

Flatt and Houst (2001) proposed that the behaviour of the superplasticizer in the cement paste is made up of three components, which was later supported by Banfill (2003) and Yamada et al. (2006). The first part of the behaviour is the absorption of superplasticizer by intercalation (i.e., the incorporation of molecules of superplasticizer into the precipitates formed as the cement hydrates), co-precipitation (i.e., precipitation of tiny solid nuclei of the superplasticizer along with the precipitation of the cement hydrates) or micellization (i.e., groups of polymer molecules are trapped within the hydrating cement making them unavailable for active dispersion), leading to the formation of an organo-mineral phase (Banfill, 2003). These phenomena that occur during the formation of ettringite and C-S-H decrease the amount of admixture available for dispersing the flocs of cement later on. Consequently, for the same superplasticizer dosage, a cement-admixture combination with a high degree of absorption will yield less fluidity than another system with a lower degree of absorption. Nevertheless, the consumption of the superplasticizer by absorption is generally small, especially when the superplasticizer addition is delayed (i.e., the superplasticizer is added at least one minute after the addition of water to the cement) (Banfill, 2003).

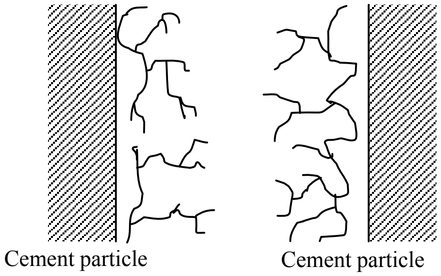
The second part of the superplasticizer is adsorbed on the cement particles, resulting in their dispersal due to the formation of an electrical double layer and consequent electrostatic repulsion between the particles. The chemical nature of the cement compounds that form the solid particle makes them undergo ionisation on the surfaces that are in contact with water. The electrical double layer (Uchikawa et al., 1997; Young, 2008) appears as a consequence of the adsorption of anionic molecules of superplasticizers on the cationic cement particles. The organic superplasticizer molecules, having charged groups (SO_3^-, COO^-) interact with the particle surfaces, imparting negative charges to the mineralogical phases of cement (see Figure 2.2a), which results in the electrostatic repulsive forces (Aïtcin, 1998; Rixom and Mailvaganam, 1999; Yoshioka et al., 2002). Mollah et al. (1995) extended the double layer theory by considering that the cement particle is covered by a layer formed by Ca^{2+} ions resulting in a trilayer of a "diffuse ion swarm", which also delays the hydration reactions. Due to the dispersive action of the superplasticizer, water that would be otherwise entrapped within the flocs is released for providing fluidity to the paste. In other words, the presence of the superplasticizer reduces the amount of water needed for the effective dispersion of the cement particles. This type of action is observed in the cases of lignosulphonates, melamines and naphthalenes. The electrostatic repulsion generated depends on the composition of the solution phase and the adsorbed amount of the superplasticizer (i.e., greater the adsorption, better the repulsion and higher the fluidity) (Nakajima and Yamada, 2004). As the electrostatic potential diminishes, flocculation of cement particles occurs and the cement paste eventually loses fluidity.

Another type of physical interaction, also based on adsorption, that is observed in the case of polycarboxylates, in addition to electrostatic repulsive forces, is that the side chain polymer molecules cause steric hindrance between the cement particles, preventing flocculation and resulting in their dispersion (Rixom and Mailvaganam, 1999; Corradi et al., 2005; Collepardi, 2005) (see Figure 2.2b). The steric repulsion depends on the length of main chain, and the length and number of side chains

(Yamada et al., 2001; Sugiyama et al., 2003). This action last for a longer time than the electrostatic repulsion and hence leads to better performance.



(a) Electrostatic repulsion



(b) Steric hindrance
Fig. 2.2 Physical action of superplasticizers (Aïtcin, 1998)

When electrostatic repulsion is the main mechanism of dispersion, the zeta potential represents a measure of the electrostatic interaction between the cement particles. The superplasticizer, being anionic, leads to a higher negative zeta potential that results in strong superplasticizer adsorption (Krishna, 1993, 1996; Houst et al., 1999a). It should be noted that the different phases of cement have differences in zeta potential (Yoshioka et al., 2002) that result in preferential adsorption of the superplasticizers on some phases such as C_3A. Similarly, the zeta potentials of early hydration products can differ and influence the adsorption of the superplasticizer (Plank and Hirsch, 2007). For example, the zeta potential of ettringite is more positive than that of calcium monosulphate (Plank and Hirsch, 2007), which causes more superplasticizer to be adsorbed on the former. Nevertheless, the maximum amount of superplasticizer adsorbed, in addition to the zeta potential, is also dependent on the type and morphology of the phase or hydration product. Accordingly, Jolicoeur and Simard (1998) and Ramachandran (2002) have determined that the amount of superplasticizer adsorbed on the monosulphate is higher than on the ettringite (though the zeta potential of the latter is higher), probably due to the higher surface area of the former.

The scientific literature on superplasticizer actions generally associates the fluidity of the paste with the amount of superplasticizer adsorbed by the cement grains. It has been stated that optimal fluidity of the paste occurs when the maximum adsorption is reached on the cement surfaces (Houst et al., 1999a; Roncero, 2000; Griesser, 2002). As mentioned earlier, the maximum adsorption depends on the chemical composition of the cement, as well as the chemical structure of the superplasticizer. It should be noted that when a higher amount of superplasticizer is adsorbed, there is better initial fluidity but the fluidity may not be maintained sufficiently over time (Nkinamubanzi et al., 2000; Li et al., 2003; Corradi et al., 2005). In such cases, the dosage of the superplasticizer has to be increased to provide an additional amount for maintaining the fluidity.

In addition to the physical effects of the adsorption, there are chemical reactions between the adsorbed superplasticizer and cement grains that occur mainly at the most reactive sites of cement particle surface (Jolicoeur and Simard, 1998). For example, polynaphthalene sulphonate reacts with C_3A in competition with SO_4^{2-} ions. Jolicoeur and Simard (1998) further points out that many organic admixtures solubilize the ionic species, through association or complexation, which delays the precipitation of the hydrated products. Also, the presence of organic molecules in the solid solution inhibits crystal nucleation, and causes slower growth of the hydration products and a change in their morphology. This is attributed to the blocking of the pores or gaps in the initial protective hydrate or the inhibition of the more reactive sites by the low molecular weight superplasticizer molecules, as shown in Figure 2.3.

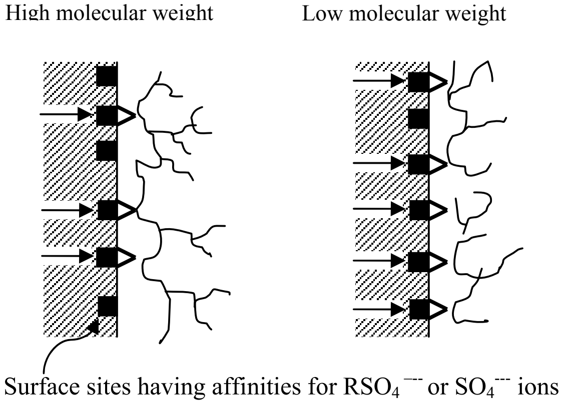


Fig.2.3 Chemical action of superplasticizers (Aïtcin, 1998)

Furthermore, Gaidis and Gartner (1991) suggest that the strong adsorption of the superplasticizer on the cement grain affects the surface charge that exerts an immediate deactivating effect on the C_3A, which helps in fluidifying the cement paste. However, after the admixture is completely removed from the solution, the C_3A resumes a more normal hydration.

The third part of the superplasticizer is non-adsorbed species that may be adsorbed subsequently maintaining the dispersion of cement particles leading to flow retention. The unadsorbed molecules also lead to additional mechanisms of action of the superplasticizer including the dispersion of cement particles by reducing the surface tension of the mixing water, the decrease in frictional resistance owing to the lining-up of linear polymers along the flow direction, and the lubrication produced by the low molecular weight polymers between the particles (Uchikawa et al., 1995; Tanaka et al., 1999).

Furthermore, some additional mechanisms supposedly enhance the performance of PCEs in terms of flowability and segregation resistance, as discussed by Tanaka et al. (1999). The ingress of non-adsorbed low molecular weight superplasticizer molecules between the cement grains causes additional dispersion due to volume repulsion (depletion effect) whereas the higher molecular weight polymers that cannot ingress between the cement particles coagulate (depletion coagulating effect) to improve the segregation resistance. Even the higher molecular weight fractions may not be completely adsorbed on the cement surface beyond a certain critical concentration (called as the critical micelle concentration for surfactants; Porter, 1994) giving rise to the effects given above.

The formation of air bubbles in the cement paste due to the incorporation of the superplasticizer can also help in its fluidification but also could reduce the strength and durability if the air content is high. The different types of admixtures have differing influences on air entrainment in concrete (Mailvaganam, 1999; Rixom and Mailvaganam, 1999; Ramachandran, 2002). Lignosulphonates incorporate significant amounts of air, which limits their dosage in concrete, in addition to other reasons already discussed earlier. The SNF and polycarboxylates can also incorporate air in the concrete due to which deairing agents are sometimes added to the commercial product. The SMF based superplasticizer, on the other hand, does not have any significant air entraining effect. Nevertheless, some of the air entrained due to the admixture incorporation is released when the concrete is vibrated, especially when it is highly workable.

2.3.3 Factors Affecting the Cement-Superplasticizer Interaction

Though there is significant knowledge about the mechanisms of action of superplasticizers, there still exist gaps in the comprehension of why occasionally these chemicals do not work as intended. This is generally termed as incompatibility between the cement and superplasticizer; the term incompatibility refers to the adverse effect on the performance when a specific combination of cement and superplasticizer is used. Common problems of incompatibility include rapid setting, delayed setting, rapid slump loss, improper strength gain, etc. These problems can in turn affect the productivity in the construction site and the hardened properties of concrete, primarily strength and durability.

The cement-superplasticizer interactions have many dimensions. On the one hand, there is the influence of the type of superplasticizer, and at the other end of the spectrum are the effects of the composition of cement, particularly the relative proportions of C_3A, alkalis and C_3S in the cement. In addition, the type of gypsum incorporated in the cement (gypsum, hemihydrate or anhydrite) has an important role to play. The fineness of cement could also affect its compatibility with a particular admixture. It is, therefore, necessary to understand the factors governing the interactions and the reasons for incompatibilities. This is all the more important since the type and number of superplasticizers available in the market has increased, along with the use of high superplasticizer dosages. The various factors affect cement-superplasticizer interactions are discussed in further detail in the following sections.

2.3.3.1 Effect of Chemical Structure of Superplasticizer

The type and dosage, degree of polymerization, degree of sulphonation, the position of functional group in the benzene ring, the molecular weight distribution of the polymer, the addition rate and the time of addition of superplasticizer influences the interaction between cement and sulphonate based superplasticizers, namely, SMF, SNF and LS (Aïtcin et al., 2001).

In the case of the lignosulphonates (Mollah et al., 1995; Rixom and Mailvaganam, 1999), the presence of low molecular weight constituents is known to cause excessive air entrainment leading to loss of strength. In addition, the high sugar content of these admixtures could cause unnecessary retardation, especially at high dosages. A further unpredictability might arise depending on whether the lignosulphonate is a sodium or a calcium salt; Ramachandran (2002) states that the sodium lignosulphonate as a better plasticizer than calcium lignosulphonate. This difference in effectiveness may be due to the presence of alkalies or due to the higher solubility of former. In order to be more effective, lignosulphonates are modified - the sugars are removed by fermentation, and low molecular weight matter is removed by centrifuging - and used as superplasticizers. Lignosulphonate admixtures easily produce a complex salt with Ca^{2+}, thus decreasing the Ca^{2+} concentration in the liquid phase, resulting in a delay in the hydration of alite and causing set retardation.

The effect of superplasticizer on the fluidity is related with adsorption and zeta potential, as mentioned earlier, which in turn depends on the molecular weight of polymer. There is no consensus, however, on the exact relations among the molecular weight, adsorption and effectiveness in terms of dispersion. Andersen et al. (1987) suggested that superplasticizer with smallest molecular weight is the most adsorbed whereas the polymer that is least adsorbed gives the highest negative zeta potential. Later, Basile et al. (1989) reported that the effectiveness of SNF in increasing the fluidity is increased when the monomer content is reduced and molecular weight is increased. They also found that the polymers with higher molecular weight caused more retardation of the cement hydration at early ages. Similarly, Bonen and Sarkar (1995) suggested that SNF with higher molecular weight led to more fluidity and retardation in setting. Rixom and Mailvaganam (1999) have clarified that for SNF, the influence of its molecular weight on the rheology, as well as the hydration of the cement paste, depends on the alkali content of the cement. In the case of high alkali cement, SNF superplasticizers with higher molecular weight (e.g., 16000 g/mol) yield better fluidity in the cement paste due to the higher surface charge provided by the larger molecules leading to higher adsorption (Kim et al., 1999; Kim and Aïtcin, 2003; Page et al., 1999). For low alkali cement, an SNF with high molecular weight does not retard the setting significantly but the incorporation of a lower molecular weight results in a considerable increase in the induction period, possibly due to lower adsorption of the latter (Rixom and Mailvaganam, 1999).

Another factor affecting SNF effectiveness is the location of the sulphonate ($-HSO_3$) group in the naphthalene structure. It is well accepted that the presence of the sulphonate group in the β-position leads to a high polymer charge and better electrostatic repulsion (Aïtcin, 1998). So, the degree of sulphonation is an important parameter for the effectiveness of the SNF based superplasticizer.

The action of SMF based superplasticizers is similar to that of SNF based products. Nevertheless, there are some differences. The adsorption characteristics of SMF based superplasticizers are such that they have higher affinity for C_3A than C_4AF and C_3S (Ramachandran et al., 1998). The stability of SMF appears to vary with the temperature and could be reason why it is not widely used, especially in countries with warmer climates. Torresan and Khurana (1998) state that if the SMF is stored at

20°C, it could have a shelf life of more than 1.5 years whereas at 40°C, its shelf life is reduced to 5-7 months. This is attributed to further condensation at higher temperature and consequent increase in viscosity.

In the case of polycarboxylates, the backbone chain consists of acrylic or methacrylic copolymers and various functional groups (polar or ionic, carboxyl or hydroxyl groups) can be grafted on the backbone chain as side chains (e.g., polyethyleneoxide graft chains). PCE type superplasticizers with high molecular weight (1400-88000 gm/mole) can be obtained with sizes of upto 30-150 nm (Uchikawa, et al.,1997). However, it appears that the normal length of main chain is 20 nm and that of the side chain is 7 nm (Ohta et al., 2000; Sakai et al., 2003). The variations in the type and length of the main and side chains of the PCE type superplasticizers have yielded a broad variety of new products with very different properties (Yamada et al., 2000; Maeder and Schober, 2003; Magarotto et al., 2003; Sakai et al., 2003; Sugiyama et al., 2003; Houst et al., 2005).

The differences in the molecular structure influence the amount of adsorption as well as the initial rate of adsorption of PCE, which in turn affect the initial fluidity and flow retention (Uchikawa et al., 1997; Maeder and Schober, 2003; Sugiyama et al., 2003; Yamada and Hanehara, 2003). In general, higher molecular weight and reduction of fractions with lower molecular weight leads to better flow in pastes (Magarotto et al., 2003). Recently, Winnefeld et al. (2007) have proposed the use of lower side chain densities and shorter side chains to obtain higher fluidity through better adsorption, and the use of longer side chains for reducing the set retardation, implying that the optimization of the molecular weight distributions is needed for the best performance. They have also stated that polymers with higher charge density are adsorbed more strongly and, consequently, result in better initial fluidity. For comb-type PCE-based superplasticizers, the charge density is higher when more free carboxylic groups are present (Winnefeld et al., 2007). The Table 2.5 summarises the relations between the structural factors of the PCE and the dispersibility parameters (Sakai et al., 2003; Sugiyama et al., 2003).

The adsorption of PCE could also depend on the amount of superplasticizer available in the solution, and consequently on the dosage of superplasticizer. More precisely, at low dosages, all fractions of the polymer are adsorbed whereas beyond a certain dosage, only fractions of superplasticizer with larger molecular weights will be preferentially adsorbed (Flatt et al., 1998; Winnefeld et al., 2007). This can lead to differences in the effectiveness of different products since they could have fractions of varying molecular weights and larger molecular fractions of varying effectiveness, especially when steric repulsion is the dominant mechanism, as shown in a study of Na-polycarboxylate-polysulphonate superplasticizers by Flatt et al. (1998).

Table 2.5 Structural aspects of the PCE that affect the fluidity of cement paste

Parameter	Structural aspects		
	Relative chain length of back bone polymer	Relative side chain length	Relative number of side chains
Low dispersibility and short dispersibility retention	Long	Short	Large
High dispersibility	Short	Long	Small
Long dispersibility retention	Shorter	Long	Large

Compared with the polycondensates (SMF and SNF), the PCE based superplasticizer is adsorbed much less due to its lower charge density (Houst, et al., 2005; Plank and Hirsch, 2007). This is attributed to the fact that the functional groups of the PCE type superplasticizers are weaker acids compared to sulphonate groups containing SMF and SNF type superplasticizers, and therefore, PCE type superplasticizers are weaker electrolytes and show a lower electronic activity. Among the polycarboxylates, adsorption is more when the charge density is higher, giving better initial fluidity.

Generally, there is a problem in achieving high initial fluidity and maintaining the same over a long period of time when using products that are currently available in the market. Consequently, it has been suggested that the combination of polymers with different rates of adsorption could lead to the retention of high slump in concrete. Corradi et. al. (2005) have used this concept in the development of new PCE-based superplasticizers that are supposed to have both water reduction and flow retention properties. This is attributed to the addition of a new functional monomer that has a lower adsorption rate than the more conventional component.

Furthermore, the response of the superplasticizers to the variation in chemical composition of cement also depends on the type of superplasticizer. According to Nkinamubanzi and Aïtcin (2004), the polycarboxylate based superplasticizer is less sensitive to the alkali and soluble sulphate content of the cement than sulphonated superplasticizers such as lignosulphonates and SNF. Further details about the dependence of the chemical composition of the cement on the cement-superplasticizer interaction are given in the following sections.

2.3.3.2 Effect of Calcium Sulphate

In order for normal set to occur in cement paste, sufficient amounts of soluble sulphate and calcium ions should be available in the solution to form calcium aluminosulphate (ettringite). When gypsum is incorporated in the portland cement there is, generally, enough soluble sulphate for hydration to proceed normally.

However, if the gypsum is replaced partially or completely with natural anhydrite, compatibility problems like rapid set and accelerated slump loss can occur especially in pastes with low w/c and with superplasticizers having sulphonate functional groups and polycarboxylates (Dodson and Hayden, 1989; Jiang et al., 1999; Mailvaganam, 1999; Nkinamubanzi and Aïtcin, 2004). This is because the rate of solution of natural anhydrite is slower than gypsum and it is further reduced possibly due to the adsorption of superplasticizer on the surface of natural anhydrite particles (Jolicoeur and Simard, 1998; Hanna et al., 2000; Ramachandran, 2002). Consequently, the availability of soluble sulfate ions in the aqueous phase is not sufficient to keep up with that needed by the C_3A, resulting in the stiffening of the cement paste due to accelerated setting caused by the formation of monosulphate, which is converted later to ettringite (Jolicoeur and Simard, 1998). Such incompatible behaviour is not expected to occur when hemihydrate or soluble anhydrite or gypsum is used in the cement since their solubility rates are not reduced by the addition of superplasticizer (Dodson and Hayden, 1989). However, Fernon et al. (1997) report that, in lime saturated solution, Na-SNF enhances the solubility of gypsum and hemihydrates significantly and that of the anhydrite only slightly, whereas the Ca-SNF does not affect the solubilities except that of the anhydrite, which is decreased. The increased solubility of gypsum or hemihydrates in the presence of Na-SNF is attributed to the formation of calcium ion complexes by the ionized sulphonates in an alkaline medium.

Since the adsorption of the superplasticizer on the C_3A and AFm is much more than on ettringite, in competition with the SO_4^{2-} ions, a sufficient amount of superplasticizer is, consequently, not available in the solution for providing fluidity to the paste. This results in the loss of fluidity or an increase in the superplasticizer demand to compensate for this effect (Jolicoeur and Simard, 1998; Ramachandran, 2002). Alternatively, the superplasticizer dosage needs to be increased to provide sufficient superplasticizer in solution so that paste fluidity is adequate. Fernon et al. (1997) also caution that an excess of dissolved calcium sulphate can lead to rapid slump loss due to the alteration of the hydration process because the formation of ettringite is inhibited.

In India, there is an increasing tendency to use synthetic gypsum instead of natural gypsum during cement production. This is because of the better quality and higher SO_3 content of synthetic gypsum. However, the rate of solubility of synthetic gypsum, and its effects on the initial adsorption and consequent fluidity, are not clear from literature and have to be investigated. Moreover, synthetic gypsum could contain soluble phosphates (in the range of 0.08-0.18 %) that increase the setting time from 3 to 10 hours (Hewlett, 2004). Such retardation can be eliminated if the phosphogypsum is neutralized with lime, and content of water soluble phosphates and fluorine is reduced to below 0.02% (Hewlett 2004; Diop et al., 2005).

2.3.3.3 Effect of Soluble Alkalis

The alkali compounds have an active role in the adsorption and consequently in the interaction. It has been observed that a higher alkali content in the aqueous solution of cement paste increases the solubility of sulphate ions and hence decreases the loss of fluidity with SNF due to lower initial adsorption of the superplasticizer (Dodson and Hayden, 1989; Chandra and Bjornstrom, 2002b). Note that the soluble alkali content is not necessarily related to the total alkali content of the cement. If cement has low soluble alkali content, the adsorption of SNF will be more and that remaining in solution will be less resulting in loss of fluidity (Dodson and Hayden, 1989;

Nkinamubanzi et al., 2000). This is because the superplasticizers act as sulphate ion providers and interact with C_3A instead of dispersing it. Consequently, cements with high alkali contents are expected to have good slump retention and to be more robust than cements with low alkali contents, when used in combination with SNF (Nkinamubanzi and Aïtcin, 2004).

The problem of inadequate fluidity for low alkali cement-SNF combinations can be overcome by adding soluble alkalis, such as Na_2SO_4 (Jiang et al., 1999; Li et al., 2003; Spiratos et al., 2003); Jiang et al. (1999) reports that 0.4-0.5% Na_2O soluble equivalent is the optimum soluble alkali content in the cement to maximize initial fluidity and to minimize the loss of fluidity. However, the addition of sodium sulphate could increase the incompatibility problem with some polysulphonates, as it alters the formation of the ettringite (Li et al., 2003).

In the case of the PCE, the excess of alkali sulphates results in the lowering of fluidity due to the shrinking of the side chains, thereby decreasing the steric repulsion (Hanehara and Yamada, 1999). Also, efflorescence problems are observed when naphthalene and melamine based superplasticizers are used with cements having high alkali oxide contents ($Na_2O + K_2O > 0.75\%$) (Akman and Cavdar, 1999).

2.3.3.4 Effect of C_3A

The interaction of the superplasticizer with the C_3A phase of the cement has the prime influence on the rheological properties of the fresh mix due to its higher positive zeta potential and reactivity compared to other cement compounds. The C_3A content or more specifically SO_3/C_3A ratio and the reactivity of C_3A controls the adsorption of the superplasticizer, which in turn affects the early hydration behaviour and workability of cement paste (Aïtcin et al., 2001). The calcium sulphate reactivity determines the availability of soluble sulphates whereas the C_3A reactivity determines the rate of consumption of these ions. Therefore, the amount of soluble sulphates along with the reactivity of C_3A influences the hydration reactions of the aluminate phases resulting in the setting of cement paste as either normal, quick, flash or false set as described by several authors (Mehta and Monteiro, 2005; Spiratos, et al., 2003).

The effect of the superplasticizer on C_3A hydration depends on the type of superplasticizer; the adsorption of SNF and SMF based superplasticizers retard C_3A hydration and delay the conversion of ettringite to monosulphonate. This is because C_3A and C_4AF surfaces rapidly adsorb large amounts of SNF and SMF. Also, in the presence of sulphate ions, the SNF forms an organo-mineral compound with C_3A and alters the morphology of the hydration products. However, high molecular weight SNF shows less retardation of C_3A than that with lower molecular weight (Rixom and Mailvaganam, 1999).

The interaction of PCE with C_3A depends on the form of C_3A, cubic or orthorhombic, with the orthorhombic form being more reactive than cubic form. Hence, a high cubic C_3A content results in low flow retention as the PCE will be adsorbed first on the C_3A surface and the ettringite will be formed later. Later, the admixture will be covered by the hydrated products and will not be available for further flow retention (Magarotto et al., 2003).

In the case of cements with less C_3A, adsorption of the superplasticizer will be more on the C_3S and C_2S, preventing their hydration, resulting in the reduction of early strength (Roberts, 1995). Also, crystallization of gypsum needles and consequent false set could occur if the C_3A content is not enough to consume the dissolved sulphates (Ramachandran, 2002). The C_3A phase in cement has very high surface area compared to its hydration product, ettringite, and consequently adsorbs large amounts of admixture resulting in loss of fluidity. Hence, the delayed addition of superplasticizer is advantageous as the hydration of C_3A takes place and ettringite is formed before the superplasticizer is added (Roberts, 1995).

2.3.3.5 Other Factors Affecting the Cement-Superplasticizer Interaction

There are several other factors that can influence the effectiveness of the superplasticizer and the interaction between the superplasticizer and cement, in general. Some important factors that have not been discussed earlier are explained in the following paragraphs.

The specific surface area influences the effectiveness of the superplasticizer since it increases the water demand, as well as the amount of superplasticizer for a given workability. Hence, the amount of superplasticizer adsorbed depends on the fineness, with finer cements leading to higher superplasticizer dosages (Aïtcin, 1998; Jolicoeur and Simard, 1998; Erdogdu, 2000; Vikan et al., 2007).

As is well known, the w/c ratio affects the performance of superplasticizer in terms of the flow of the cement paste and workability of concrete. Moreover, most of the incompatibility problems occur at low w/c, where the lower interparticle separation between the cement particles makes the system to be more sensitive to the loss of water by evaporation or hydration reactions resulting in higher loss of fluidity with time (Collepardi, 1998).

The placing of concrete in different environmental conditions also affects the superplasticizer performance. Temperature is the major environmental factor affecting cement-superplasticizer interaction. Generally low temperatures decrease the fluidity, which cannot be compensated with the addition of superplasticizer beyond the saturation dosage (Gettu et al., 1997; Roncero et al., 1999). On the other hand, high temperatures increase superplasticizer adsorption, which increases the initial fluidity and increases the superplasticizer demand for flow retention over a certain range of temperatures (Roncero et al., 1999; Greisser, 2002). Also, the temperature increase causes an increase in the reactivity of C_3A, which causes a more rapid loss of fluidity and formation of higher ettringite contents with finer morphology in the presence of superplasticizer (Greisser, 2002; Spiratos et al., 2003).

The effect of temperature on mixes with PCE based superplasticizers is dependent on its chemical structure (e.g., the carboxylates have the highest fluidity loss compared to other functional groups) (Felekoglu and Sarikahya, 2007; Grzeszczyk and Sudol, 2005), with the increase in temperature leading to a lower increase of flow in the paste and lower flow loss for longer polyethylene oxide graft chains (Nawa et al., 2000). This is attributed to the higher adsorption of the graft chains with an increase in temperature, as a result of which the steric repulsion of the longer graft chains is less affected.

Roncero et al. (1999), Roncero (2000), and Fernandez-Altable and Casanova (2006) have shown that though the fluidity increases with the temperature, it has no practical effect on the saturation dosage of superplasticizer, which is attributed to the dependence of the saturation on the available surface area of the cement particles.

2.3.4 Effect of Superplasticizer on the Morphology of Hardened Cement Paste

The morphology of the hardened cement paste could be affected by the alteration of the cement hydration reactions by the retarding effect of the superplasticizers as well as the intercalations with the early hydration products, as described in the previous sections. The polysulphonates, can combine with the interstitial phase of the cement

(C_3A+C_4AF) to form an organo mineral composite resembling ettringite (Aïtcin et al., 2001). They could also modify the morphology of ettringite produced during hydration; i.e., ettringite crystallizes in small and thick crystals rather than conventional needle shaped crystals (Aïtcin et al., 1994; Hanna et al., 2000; Prince et al., 2002). The addition of superplasticizer also modifies the morphology of the portlandite; i.e., the size of portlandite crystals decrease and also their form changes from block-like to thin plates (Grabiec, 2004).

In addition to modifying the morphology, the delay in the release of SO_4^{2-} (due to the presence of anhydrite) results in the formation of monosulphoaluminate, first and then ettringite is formed (Prince et al., 2003). The addition of lignosulphonates further reduces the solubility of anhydrite due to the reduction in the rate of diffusion of ions at solid-liquid interphase, and further promotes this phase transformation (Prince et al., 2003).

In general, the change in morphology due to the incorporation of superplasticizer improves the rheological properties by yielding smaller hydrate particles and preventing hydration products from bridging neighbouring cement particles. This results in substantial reduction in the yield stress of paste and increase in fluidity. There is also a difference in porosity and pore size distribution of superplasticized concrete compared to normal concrete. Cements with high C_3A and low SO_3 content have larger pores that decrease in size with higher SO_3 contents whereas the pore size in low C_3A cements is independent of the SO_3 content. Generally, higher numbers of smaller pores are produced in superplasticized mixtures (Roncero, 2000; Khatib and Mangat, 1999). This has been attributed to better silicate polymerization leading to the refinement of pores and consequent reduction in porosity (Puertas et al., 2005).

2.3.5 Effect of Superplasticizer on Properties of Concrete

As intended, the incorporation of superplasticizers increases the workability of concrete that permits the use of comparatively lower w/c leading to higher strengths. In addition to strength, the properties of concrete that are affected include slump, air content, bleeding, segregation and setting time in the fresh state, and properties like permeability, abrasion resistance and durability in the hardened state. The type of superplasticizers and cement can cause variations in these properties and in certain cases the incompatibility between the two leads to adverse effects like loss of fluidity, retardation in setting, air entrainment and reduction in strength gain, as explained in the previous sections. Aïtcin et al. (2001) observed that cements with a C_3A content of 6% to 10%, a soluble alkali content of 0.4 % to 0.5% give cement-polysulphonate combinations that are both compatible and robust.

Concrete with high workability containing a superplasticizer generally shows more rapid slump loss than that with the same workability and without superplasticizer. This could be attributed to the loss of consistency due to the low w/c during the dormant stage and the increased adsorption of the superplasticizers by the aluminate phase (Ramachandran et al., 1998). In addition, the higher slump loss is related with the C_3S phase of cement also; i.e., the hydrate coatings restore charge interactions between the C_3S grains, thereby restoring the tendencies for flocculation (Ramachandran, 2002). Redosing of the superplasticizer neutralizes these charges and restores the fluidity, but continued hydration will lead eventually to slump loss.

In a superplasticized concrete, generally no segregation or bleeding is expected to occur at the saturation dosage of the superplasticizer. When redosing is used to control the loss of slump, however, bleeding and segregation may occur if the second dosage is too high; overdosage of superplasticizer generally promotes segregation and formation of a white deposit containing lime, calcium sulphate and calcium carbonate on the top surface when hardened (Ramachandran, 2002).

When superplasticizers are added to concrete at the appropriate dosage, the 28-day compressive strength of superplasticized concrete is often equal or greater than the corresponding strength of the reference concrete (Rixom and Mailvaganam, 1999; Ramachandran, 2002). This is attributed to the reduction in w/c as well as the higher workability and better compaction achieved due to the incorporation of superplasticizers Dhir and Yap (1983) also reports that even though there could be some initial retardation, superplasticizers produce compressive strengths of the same order as the normal concrete at 3, 7 and 28-days. This is because, normally, the C_3A and C_4AF phases rapidly adsorb large amounts of SNF and SMF, so that only small amounts of SMF and SNF are available with the aqueous phase to retard the hydration of C_3S.

Nevertheless, there are some reports of strength reduction while using naphthalene based superplasticizers and melamine based superplasticizers, especially with cements having low C_3A content and high C_3S and C_2S contents (Ramezanianpour et al., 1995). This may be either due to higher adsorption on the C_3S and C_2S phases or gypsum crystallization and consequent false set in the absence of adequate C_3A, as reported earlier (Roberts, 1995; Ramachandran, 2002)

The creep and shrinkage of superplasticized concrete is comparable to or is less than that of reference concrete (e.g., Seung-Bum, 1999), although there are several exceptions. For the same amount of moisture loss, the superplasticized concrete could exhibit larger shrinkage which may be related to the larger dispersion of cement and cement hydrates (Ramachandran, 2002). Dhir and Yap (1983), and Gettu et al. (2002) have reported that drying shrinkage is higher for superplasticized concrete with high workability; with SNF based superplasticizers leading to higher total shrinkage than PCE based products whereas SMF based shows lower shrinkage than PCE based superplasticizers. This could be attributed to the refinement of pore structure to more number of fine pores (Roncero, 2000; Gettu et al., 2002; Roncero et al., 2002).

2.3.6 Admixture – Admixture Interaction

2.3.6.1 Cement-Superplasticizer Interaction in the Presence of Mineral Admixtures

Supplementary cementitious materials (or mineral admixtures) are generally incorporated in concrete as a replacement for cement to reduce the heat of hydration and to enhance strength and durability. It is usually reported that the addition of mineral admixtures reduces the workability due to the higher surface area and consequently increases the water and superplasticizer demand (e.g., Agullo et al., 1999). Nevertheless, there could be some workability enhancement due to the addition of fly ash and silica fume, in low volumes, which is generally attributed to the spherical shape of the particles and consequent reduction in the interparticle friction (Ferraris et al., 2001).

The incorporation of fly ash could also affect the hydration process of cement due to the additional aluminates (of the fly ash) that suppress the silicate reaction. This retarding effect is worsened due to the lack of sulphates in the presence of superplasticizers (Roberts, 1995).

2.3.6.2 Influence of Other Chemical Admixtures on Cement-Superplasticizer Interaction

The other chemical admixtures generally used in concrete include viscosity modifying admixtures (VMA), air entraining agents, damp proofing compounds and shrinkage reducing admixtures. A viscosity modifying admixture is usually incorporated with superplasticizers to produce flowing/self compacting concrete. The interaction of the superplasticizer with the VMA depends on the mode of action by which the latter provides higher viscosity in the concrete. Most VMAs tend to increase the viscosity by forming gel/cement slurries rather than increasing the viscosity of water in the mix. The VMA molecules could compete with the superplasticizer for active sites on the cement particles, resulting in lower superplasticizer adsorption (Mailvaganam, 1999; Bedard and Mailvaganam, 2006).

The addition of a superplasticizer modifies the relationship between the air content and the spacing factor (air bubble spacing), and sometimes significantly destabilizes the air-void system (Bedard and Mailvaganam, 2005) caused by the incorporation of an air-entraining agent. For example, when a lignosulphonate based water reducer is added to concrete containing an air entraining agent, a substantial increase in air content occurs and the specific surface of air bubbles are reduced.

The combination of a shrinkage reducing admixture (SRA) with a superplasticizer reduces the efficiency of the SRA in reducing shrinkage. Also, the combination increases the retardation in setting more than the superplasticizer alone (Gopinath and Gettu, 2008).

2.4 Need for the present study

The current level of knowledge worldwide about the factors affecting the cement-superplasticizer interaction is described in this chapter. Specific issues of incompatibility have also been addressed, namely, loss of workability, alteration of setting behaviour, reduced rates of strength gain and change in the microstructure. There are contradictions regarding the influence of molecular weight and the side chain lengths of PCE on the adsorption behaviour, which have also been brought out.

In the Indian context, cement standards in our country are not very stringent, and enable manufacturers to adjust their product in many different ways. For example, while the minimum fineness is specified for different grades of cement, there is no control on the maximum values. Similarly, wide ranges in the chemical composition are acceptable. This could result in significant variability in the cement properties. Also, the alkali content, which has a major influence on cement-superplasticizer interaction, is not considered as a characteristic of the chemical composition for a particular grade of cement.

From the viewpoint of the use of superplasticizers, there is insufficient knowledge among users regarding the limitations of different types of chemicals. Users, who are unaware of compatibility issues, often suffer when the supply of cement and/or admixture has to be changed during the course of a project. Problems arising from compatibility issues are often mistaken for problems with the concrete mixture design because of the lack of information about the subject amongst practicing engineers. Admixture manufacturers try to overcome the problem by formulating project-specific chemicals, which is obviously, only a short term solution.

Cement-superplasticizer interaction in concrete is due to a complex blend of chemical and physical mechanisms that are interdependent. The complicated nature of the problem prevents the development of simple solutions to address field related issues of the application of superplasticizers. Hence, a detailed study on the cement-admixture interaction is required for optimizing different types of admixtures in a cementitious system.

Studies on cement-superplasticizer interactions in India have been limited to the workability evaluation of concretes containing these chemicals. There have not been any investigations to understand the physico-chemical nature of this interaction. Thus, the results from such studies are not broad-based, i.e. they apply to a small group of cements and/or chemical admixtures. There is a distinct need for a study of the interaction of Indian cements and admixtures, as well as to select an appropriate dosage of the superplasticizer. Moreover, the wide range of cements used, varying transportation durations and climatic conditions necessitate fundamental studies that can explain the mechanisms of interaction and help establish methods for identifying incompatibilities in practical situations.

Simple methodologies are required to identify these incompatibilities due to such interactions and to further understand the fundamental nature of admixture behaviour in cement-based systems. The understanding of these interactions should be both at the applications scale (for example, studying flowability and retention of workability in pastes and concretes, retardation in setting), as well as at the micromolecular scale, where some insight can be obtained into the physico-chemical interactions between cement particles and superplasticizer molecules.

CHAPTER 3

STUDY OF THE FLOW BEHAVIOUR OF SUPERPLASTICIZED CEMENT PASTE

3.1 GENERAL

A brief description about the cement hydration reactions and the influence of superplasticizers on the hydration reactions, morphology of hydrated products and the properties of superplasticized concrete has been presented in the previous chapter. In addition to providing good workability, the superplasticizer also influences the slump retention and setting process. The interaction between the cement and superplasticizer governs the flow behaviour of concrete. To study this interaction, it is proposed to analyse the flow of cement paste with simple methods like Marsh cone and mini-slump tests, and more fundamental tests like those with a viscometer.

The basic objective of this chapter is to formulate the methodology for studying the fluidity of superplasticized cement pastes that will be used in the more detailed studies in the rest of the thesis. The specific objectives are

- To select a suitable mixing method for preparing the superplasticized cement paste that is representative of the paste phase in concrete.
- To validate the suitability of simple test methods, such as the Marsh cone and mini slump tests, for studying the flow behaviour
- To understand the significance of results from simple methods with regard to rheological parameters.

In order to meet the above objectives, the influence of the mixing method on the fluidity of superplasticized cement paste is studied through the Marsh cone and mini-slump tests. Subsequently, the influence of type and dosage of superplasticizer on the flow behaviour of the paste is studied. Finally, the correlations between the results obtained with the simple test methods and those obtained from viscometric studies are presented which helps to select an appropriate methodology to study the fluidity of cement paste and to understand the results from empirical tests better.

3.2 MATERIALS USED IN THE STUDY

3.2.1 Cement

Ordinary 53 grade portland cement (ASTM Type 1 Cement) (denoted as Cement 1) satisfying the requirements of IS 12269 (2004) was used in the work presented in this chapter. The chemical properties are given in Table 3.1, as determined by the National Test House, Chennai, for the sample used.

The compounds present in the cement can be quantified using the results of the chemical analysis of the clinker corresponding to the cement and the Bogue equation. Accordingly, the clinker was obtained from the cement manufacturer and tested in Holcim Roodeport Laboratory in South Africa; the results of the analysis are also given in Table 3.1. These data were used to determine the proportions of the compounds present in the cement (see Table 3.2).

From the test results (Tables 3.1 and 3.2), it is confirmed that the cement used can be considered as a low alkali cement since the $(Na_2O)_{eq}$ is less than 0.6% (Hewlett, 2004); that the SO_3 content is within the normal range (i.e., 2–3.5%) for ordinary Portland 53 grade cement and, therefore, is not expected to affect the superplasticizer adsorption significantly (Chandra and Bjornstrom, 2002a); and that the C_3A content is in the normal range (i.e., 4-8%).

Table 3.1 Chemical properties of the cement and the corresponding clinker

Characteristics	**Quantity (% by mass)**	
	Cement	**Clinker**
Calcium oxide (CaO)	60.81	63.10
Silica (SiO_2)	19.50	20.80
Alumina (Al_2O_3)	4.12	5.80
Iron oxide (Fe_2O_3)	6.06	5.30
Magnesia (MgO)	1.52	0.80
Sulphur anhydrite (SO_3^{2-})	2.48	0.68
Insoluble residue	1.51	-
Total loss on ignition	3.41	0.40
Total chloride content (Cl^-)	0.01	-
Alkali content: Na_2O K_2O $(Na_2O)_{eq}$	0.05 0.28 0.23	- - 0.20
Lime saturation factor	0.93	0.92
Ratio of alumina to iron oxide	0.68	1.09

Table 3.2 Bogue composition of the clinker

Compound	Composition (%)
C_3S	51.7
C_2S	20.8
C_3A	6.5
C_4AF	16.1

In addition to the chemical properties, it is necessary to determine certain physical properties of the cement used for characterizing its behaviour. In this work, the Blaine specific surface area, water demand for a paste of standard consistency, and the initial and final setting times were determined experimentally, as detailed in the following sections.

3.2.1.1 Determination of the Water Demand for Standard Consistency of Cement

The consistency of the cement paste is determined as per ASTM C 187 (2004)and IS 4031: Part 4: (2005), where the quantity of water found that produces a cement paste of standard consistency, defined as that which permits the Vicat plunger to penetrate upto 5 to 7 mm from the bottom of the Vicat mould. Cement pastes with varying w/c are prepared (by hand mixing) and the penetration is checked for each of them. The amount of water in the paste that satisfies the above mentioned condition is expressed as a percentage by mass of dry cement, and taken as the water demand of the cement. This can be considered as the minimum w/c needed for the paste to be homogeneously, and uniformly mixed and moulded. The water demand, obtained as an average result of 3 trials was 31% (see Table 3.3).

Table 3.3. Physical properties of cement 1 (C1)

Property	Value (mean and standard deviation)
Water demand for normal consistency of cement paste	31% (± 1.3%)
Initial setting time	106 minutes (± 7 minutes)
Final setting time	190 minutes(± 6 minutes)
Blaine specific surface area	332 m^2/kg (± 10 m^2/kg)

3.2.1.2 Determination of Initial and Final Setting Times

The initial and final setting times are determined as per IS 4031: Part 5 (2005). The cement paste is prepared with 0.85 times the water required to give a paste of standard consistency (see previous section). It is filled in the Vicat mould and the corresponding needle is allowed to penetrate through the paste. The period elapsing between the time when water is first added to the cement and the time at which the penetration of the needle is 35.0 ± 0.5 mm is taken as the initial setting time. Note that this is similar to procedure of ASTM C-191 (2001a), except that the paste used (i.e., same w/c) is of standard/normal consistency, and the penetration for the initial setting time is 25 mm.

The test is continued with a standard needle with an annular attachment for determining the final setting time. The period elapsing between the time when water is added to the cement and the time at which the needle makes an impression on the surface of the test block while the attachment fails to do so is taken as the final setting time.

The values obtained for the setting times are given in Table 3.3 as averages from three trials. As the initial setting time is more than 30 minutes and the final setting time is less than 10 hours, the IS code requirements for the setting times are satisfied. It should be noted, however, that the difference between the initial and final setting times is only about 90 minutes, which is relatively low.

3.2.1.3 Determination of the Fineness of Cement

The fineness of cement has been determined by the Blaine air permeability method as per IS 4031: Part 2 (2005) and ASTM C 204 (2007). The specific surface area obtained (332 m^2/kg) is within the limits given for a 53 grade OPC.

3.2.2 Superplasticizers

Superplasticizers for this study were selected from the four different families of products available (i.e., lignosulphonates, naphthalenes, melamines and polycarboxylates) in order to obtain representative results that would help understand the effect of the different types on the flow behaviour of cement paste. Table 3.4 gives the details of the commercial products used; the products are denoted as the abbreviation of the type followed by a number. The values of the solid content, pH, density were obtained in the laboratory as per IS 9103 (2004), and cross-checked with data from the corresponding supplier. It can be seen that the active part of superplasticizer varies from 32% to 44 % for different families as well as for the same family. The recommended dosage of the superplasticizers is also given in the Table 3.4. The superplasticizer dosages given in this work are all in terms of the solid content; the water contained in the superplasticizer has been accounted for in the water content of the mixes.

Table 3.4 Properties of superplasticizers

Designation	Chemical type	Density kg/litre	Solid content (%)	pH	Recommended dosages (sp/c %)
LS-C1	Lignosulphonate	1.18	38	7.5	0.18-0.27
SNF-S1	Polynaphthalene sulphonate	1.09	37	6.7	0.2-0.8
SNF-D1	Polynaphthalene sulphonate	1.16	32	6.8	0.22-0.74
SNF-D2	Polynaphthalene sulphonate	1.25	44	7.8	0.44-0.66
SNF-C1	Polynaphthalene sulphonate	1.20	40	7.4	0.2-0.3
SMF-S1	Polymelamine sulphonate	1.30	40	8.5	0.2-0.68
SMF-C1	Polymelamine sulphonate	1.28	38	7.0	0.19-0.3
PCE-S1	Polycarboxylate ether	1.09	38	7.5	0.08-0.33
PCE-D1	Polycarboxylate ether	1.10	33	7.4	0.07-0.3

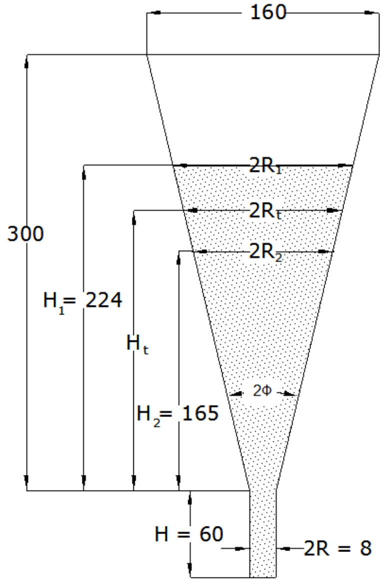
3.3 TEST METHODS USED FOR STUDYING THE FLOW BEHAVIOUR OF THE CEMENT PASTE

Due to the important functions of superplasticizers in concrete, the selection and dosage criteria are fundamental for determining the optimum composition of concrete. From the practical point of view, it is better to make this choice using the actual concrete at the construction site under the local conditions. However, tests of concrete imply significant labour, material and time. Besides, such tests do not reflect the fundamental action of the superplasticizer with regard to physical and chemical interactions. Therefore, several methods based on tests of paste and mortar have been developed for determining the optimum superplasticizer dosage in concrete.

The Marsh cone and mini slump tests are simple empirical methods to characterize the flow behaviour of cement paste whereas rheological tests with a viscometer provide more fundamental information about the material but require more complicated equipment and skilled operators. The fundamentals of these three methodologies, and the procedures adopted in this work are detailed in the following sections.

3.3.1 Marsh Cone Test

The Marsh cone (Figure 3.1) test has been used previously to evaluate the relative fluidity and the saturation superplasticizer dosage in cement pastes and mortars (de Larrard et al., 1998; Aitcin, 1998; Khayat and Yahia,1998; Agullo et al., 1999; Roussel and Roy, 2005; Royy and Roussel, 2005). In the present study, a metal cone (as per the guidelines of European standards EN 445, French standards P 18-358, which is similar to ASTM C 939 (1987), with a nozzle of diameter 8 mm was employed. An initial volume of 1000 ml of paste was poured into the cone and the time required for 500 ml of it to flow out was measured. The test gives the fluidity of the paste in terms of the flow time; higher the flow time, lower is the fluidity of the paste. The saturation point is the dosage beyond which further addition of superplasticizer does not increase fluidity significantly but can produce segregation (Agullo et al., 1999); the saturation dosage can be taken as the optimum superplasticizer dosage for a given cement paste.



R, H - Radius and length of nozzle

R_1, H_1 - Radius of the free surface and height of fluid in the cone at the initial moment

R_t, H_t - Radius of the free surface and height of fluid in the cone at any time t

R_2, H_2 - Radius of the free surface and height of fluid in the cone at the final moment

φ – Angle between the axis and the generator of the cone

Fig. 3.1 Geometry and dimensions (in millimetres) of the Marsh cone

Gomes et al. (2001) proposed a method for the objective determination of the saturation dosage based on the Marsh cone flow time curve of pastes, which is illustrated in Figure 3.2. In this method, the internal angle (α) corresponding to each data point is calculated and the superplasticizer dosage corresponding to an internal angle of 140°±10° is taken as the saturation dosage. Interpolation is used to determine the dosage when there are no data points corresponding to that range of angles. This criterion was proposed based on about 200 tests on superplasticized cement pastes (Gomes, 2002).

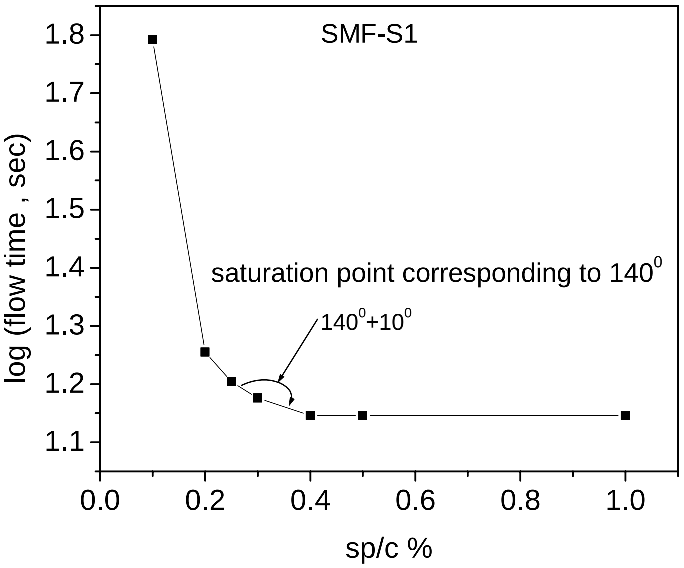


Fig. 3.2. Flow time curve showing the determination
of optimum superplasticizer dosage
(according to the method of Gomes et al., 2001)

The Marsh cone test (see Figure 3.3) can also be used to study the loss of fluidity with time, the fluidity of cement mortar, optimization of cement paste with mineral admixtures and incompatability between cement and superplasticizer (Agullo et al., 1999).

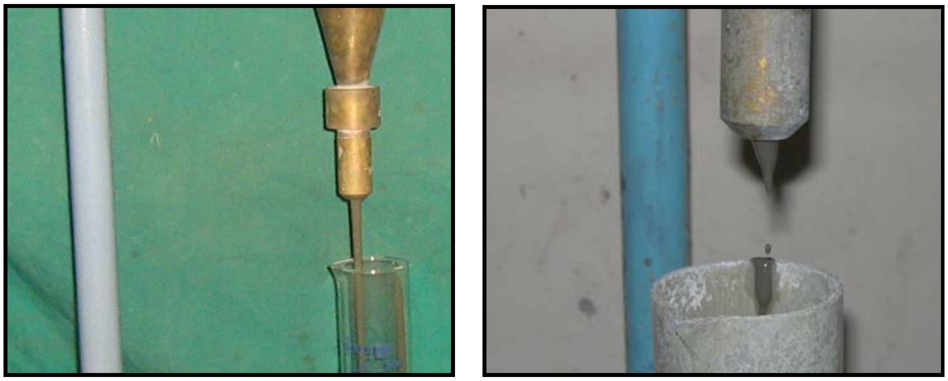


Fig. 3.3 Marsh cone test showing continuous and discontinuous flow

3.3.2 Mini-slump Test

The mini-slump test developed by Kantro (1980) has also been used to study the flow behavior of superplasticized cement paste (Aitcin, 1998; Khayat and Yahia,1998; Gomes, 2002; Roussel, 2006; Tregger et al., 2008). In this test, a mould in the shape of a truncated cone, with dimensions proportional to the Abram's cone, is filled with cement paste and the spread diameter is measured after lifting the mould. Additionally, the time taken for the paste to reach a diameter of 115 mm was also determined here. Also, visual examination helps evaluate the bleeding and segregation of the paste.

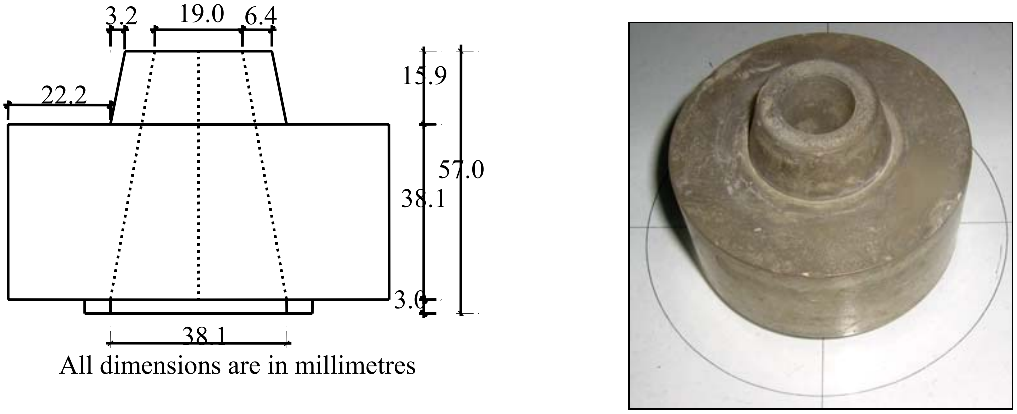
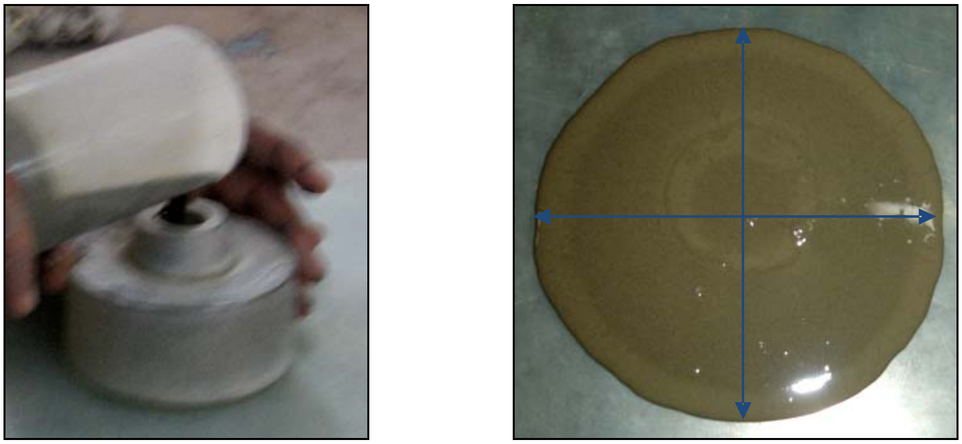


Fig. 3.4 Mini-slump cone



(a) Filling of the mini-slump

(b) Spread of the Paste

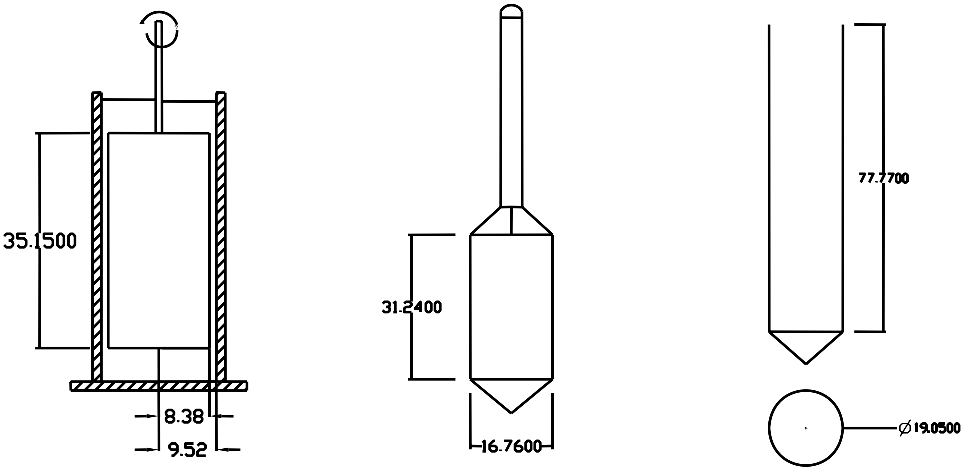
Fig. 3.5 Mini-slump test

3.3.3 Viscometer Test

Viscometer tests on cement paste can be used to study the effect of the changes in cement, type and dosage of admixtures, such as superplasticizers, on paste characteristics like yield stress and plastic viscosity (Asaga and Roy,1980; Banfill, 1981; Masood and Agarwal, 1994; Beaupre and Mindess, 1998; Claisse et al., 1999; Cyr et al., 2000; Park et al., 2005). The basic principle is to apply different shear rates to the paste in a viscometer and measure the corresponding shear stresses. Generally, a loading-unloading cycle is applied to the paste, preceded by some pre-shearing, and the response during unloading is used to determine the rheological parameters (Goisis et al., 2003; Papo and Piani, 2004). Cement paste normally exhibits shear-thinning behaviour, where the slope of the shear stress versus shear strain rate curve decreases with an increase in the shear rate. Such shear-thinning response is attributed to the structural breakdown and rebuilding that takes place in the paste (Tattersall and Banfill, 1983) with the former mechanism predominating (Lapasin et al., 1983). There are, however, notable exceptions; e.g., dilute superplasticized pastes may exhibit Newtonian behaviour while an overdosage of superplasticizers may result in shear thickening (strain-hardening) that could be attributed to the agglomeration of excess superplasticizer in the aqueous solution of the paste or segregation(Cyr et al., 2000; Papo and Piani, 2004; Lootens et al., 2004).

In the present study, a Brookfield HA DV II +Pro viscometer was used with a coaxial cylinder setup (inner cylinder radius = 16.77 mm, gap width = 1.14 mm) as shown in Figure 3.6 and Rheocalc software for programming the test. The details of the coaxial cylinder set up are shown in Figure 3.7. The rheological behaviour depends on the type of spindle, shear rate, the gap between the cylinders and environmental conditions. The basic principle of the experiment is to apply a known shear rate to the fluid through the spindle and measure the corresponding shear stress produced.

Fig. 3.6 Brookfield HA DV II +Pro viscometer (Asphalt Laboratory, IITM)



(a) Co-axial cylinder (b) SC4 21 - Spindle (c) HT-2- Sample chamber

Fig. 3.7 Details of co-axial cylinder setup

Three loading-unloading cycles were imposed by increasing, and later decreasing, the shear rate from 23 to 163 s^{-1} in seven steps. The shear history of rheological testing for one hysteresis cycle is shown in Figure 3.8.

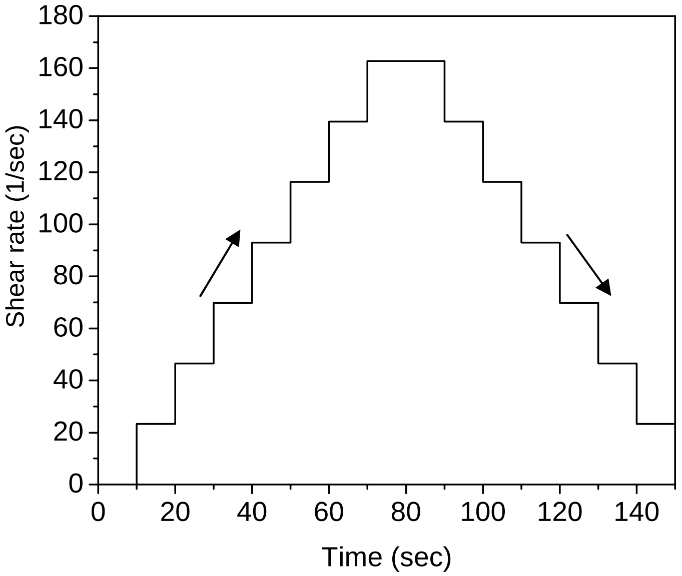


Fig. 3.8 Shear history of rheological testing

The typical response is shown in Figure 3.9, where the first two cycles are considered as pre-shearing and the downward curve of the third cycle is used for determining the rheological parameters. The pre-shearing is needed for the structural breakdown of cement paste sample and to create uniform conditions before testing.

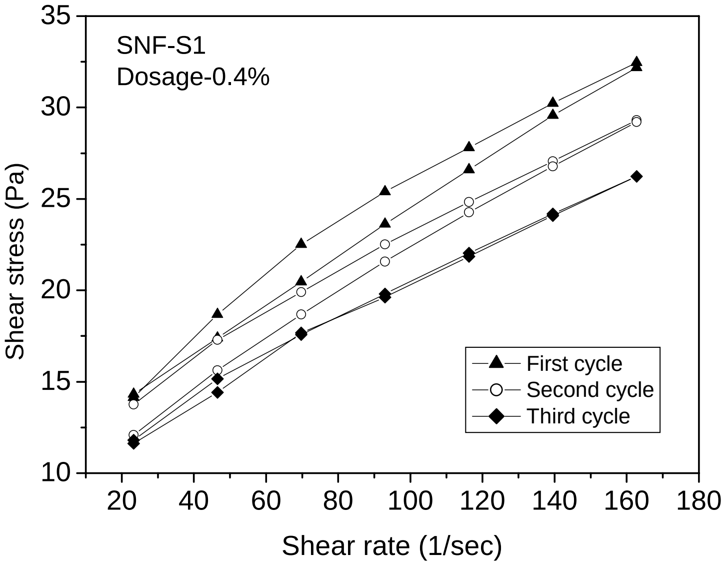


Fig. 3.9. Typical graph showing hysteresis cycles for a superplasticized cement paste

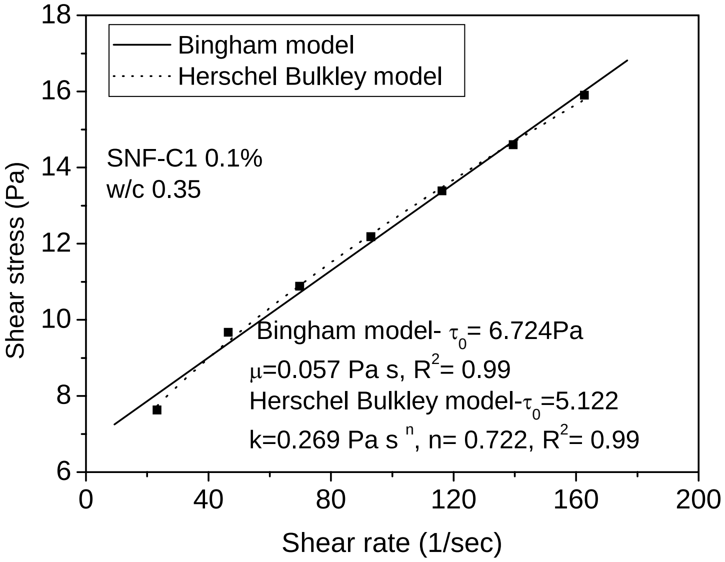
The shear stress-strain behavior of cement paste has been represented using several models (Atzeni et al., 1985; Nehdi and Rahman, 2004), the simplest of which is the Bingham model:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \tag{3.1}$$

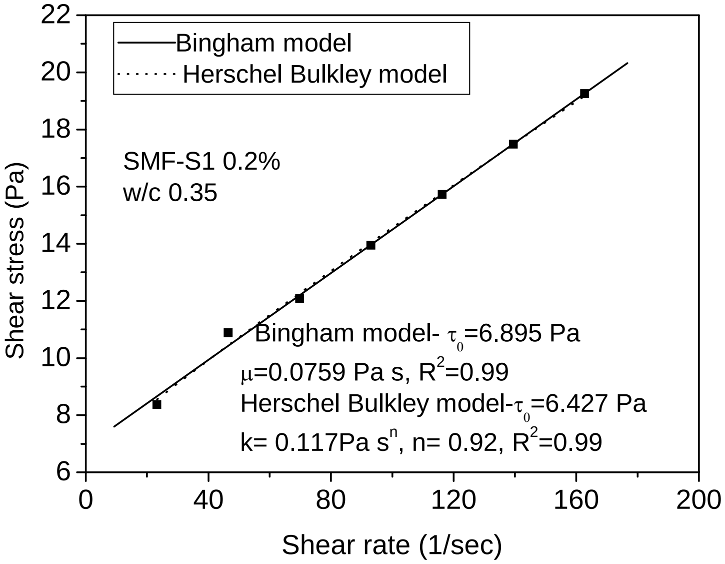
where τ is the shear stress in (Pa), $\dot{\gamma}$ is the shear strain rate (1/sec), μ_p is the plastic viscosity (Pa s) and τ_0 is the yield shear stress (Pa). The Bingham model is generally fitted to the experimental data (during unloading), as illustrated in Figures 3.10(a-c), to obtain the yield shear stress and the plastic viscosity of the cement paste. This appears to give a satisfactory representation of the rheological behaviour in most cases. Even slight shear thickening response can lead to a negative yield stress when the Bingham model is fitted to the experimental data. When the τ_0-value is negative, as in Figure 3.10c, the data are normally re-fitted by forcing the condition of τ_0=0 (i.e., Newtonian model). For these reasons, a more versatile model, namely the Herschel-Bulkley model, has been used by several researchers (de Larrard et al., 1998):

$$\tau = \tau_0 + k \dot{\gamma}^{\,n} \tag{3.2}$$

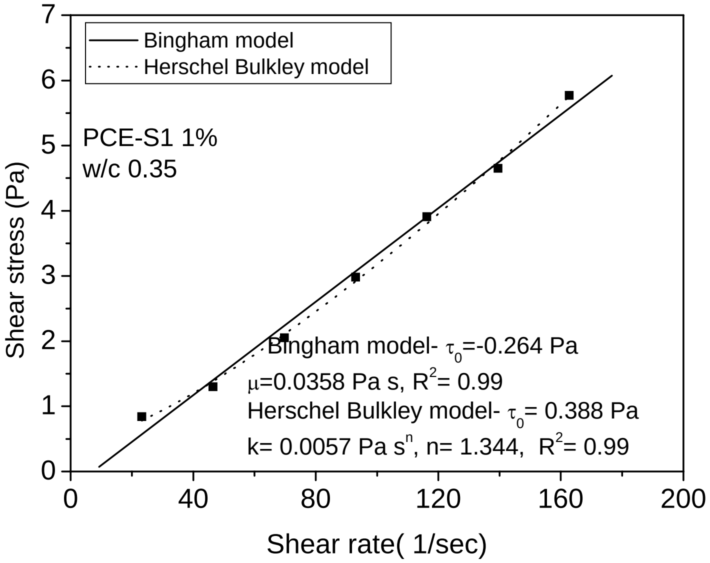
where τ is the shear stress in (Pa), $\dot{\gamma}$ is the shear strain rate (1/sec), n is the power index, k is the consistency (Pa s^n), and τ_0 is the yield stress (Pa). Since the consistency and power index are interdependent, there is no single term that represents the plastic viscosity of the material.



(a) Model parameters at less than saturation dosage



(b) Model parameters at saturation dosage



(c) Model parameters at dosage much more than saturation

Figure 3.10 Fits of experimental data with the Bingham and Herschel-Bulkley models at (a) less than saturation (b) at saturation (c) dosage much more than saturation

3.4 SELECTION OF MIXING METHOD

The purpose of concrete mixing is to achieve a uniform mixture of all material components and facilitate hydration. The type of mixer used has an influence on the mixing efficiency (i.e., degree of dispersion of cement particles) depending on whether it is intensive or extensive (Yang and Jennings, 1995). Mixing is especially important for high performance concrete (HPC) of lower binder content. The type and efficiency of mixer will influence the mixing time needed, the superplasticizer dosage required, and the quality of HPC produced (Chang and Peng, 2001). Previous studies of Yang and Jennings (1995), and Diamond (2005) have concentrated on the microstructure and rheology of pastes mixed in different ways. They have shown that intensive mixing leads to more homogeneity and better dispersion of cement particles. Also, the viscosity of the paste decreases with intensive mixing, reflecting the effectiveness of such methods (Williams et al., 1999; Ferraris, 2001).

Studies conducted by Diamond (2005) show that prolonged mixing can induce higher stiffness in the mix. Therefore, it is better to have an intensive mixing procedure of short but adequate duration instead of a prolonged mixing time.

Hence, it is important to understand the effect of different mixing methods on the fluidity of superplasticized cement paste as well as to select the type of mixing method which leads to a paste that is representative of concrete. In the present work, two simple methods, the Marsh cone and mini-slump tests, are used for studying the fluidity of cement paste made with different mixing techniques.

3.4.1 Materials Used in the Selection of Mixing Method

In the present study, tests were conducted on cement paste with water/cement ratio of 0.35. Birla Super 53 grade ordinary portland cement (OPC) and a polycarboxylic ether based superplasticizer (PCE-D1) was used. The recommended dosage of superplasticizer is 0.5-1.6 litres per 100 kg of cement. Distilled water was used for mixing the cement paste. Superplasticizer dosage, denoted as sp/c, is expressed as the ratio of solid content of superplasticizer to cement content by weight. All the test materials were kept in the environmental chamber at a temperature of 27 ºC for 24 hours prior to testing.

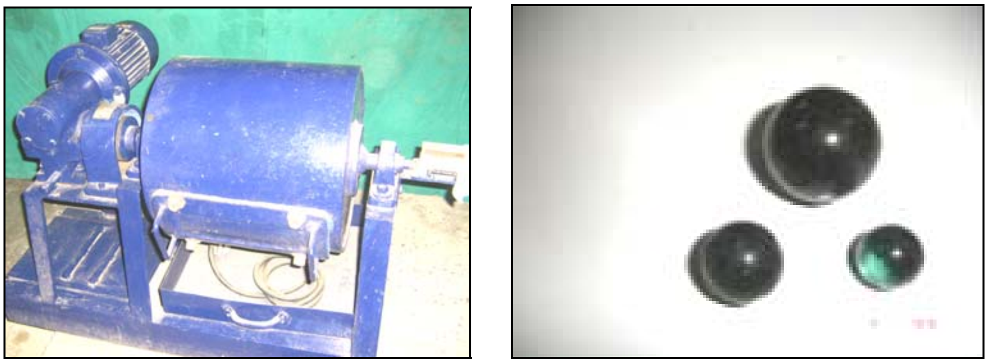
3.4.2 Experimental Details

The first paste was mixed with a Hobart mixer (1/6 hp) with a B-flat beater (Figure 3.11a) with low speed (with shaft speed of 139 rpm and planetary speed of 61 rpm), the second paste with a Hobart mixer with a D-wire whip (Figure 3.11 b) at medium speed (with shaft speed of 285 rpm and planetary speed of 125 rpm) and third with a high shear rate kitchen blender (550 watts, 16000-18000 rpm). The fourth paste was made by grinder (1/4 hp, 300 rpm) mixing and fifth by hand mixing. The mixing time of 5 minutes was selected to minimize any effects due to incomplete mixing with respect to the capability of the machine. After determining the proportions of constituents, the mixing was performed in the following sequence for all the cases. The cement and 70 % of the water required were mixed together in the mixer for one minute, and after that superplasticizer and the remaining water were added to the cement paste. This sequence of addition is preferred because the delayed addition of superplasticizer reduces the amount of superplasticizer required (see Chapter 2). In this case, the water content of the superplasticizer was deducted from the water added. The paste was mixed for 2 minutes at the same speed. The sides of mixer bowl were scraped for 15-30 seconds. Again the paste was mixed for 2 minutes.

Fig. 3.11 (a) Hobart mixer with B-flat beater (b) Hobart mixer with D-wire whip

3.4.3 Ball Milling

The study for selecting the mixing method is conducted on cement paste instead of concrete because of the reasons explained in sections 3.3 and 3.4. However to ensure that the paste is representative of the paste within the concrete, “ball milling” was done for simulating the concrete mixing through the use of steel balls or glass marbles of 27.5 mm, 17.5 mm and 12.5 mm placed in a drum along with the paste (Figure 3.12).



(a) Los Angeles abrasion testing machine (b) Glass marbles

(c) Mixing of paste with glass marbles (d) Sieving of cement paste

Fig. 3.12 Test set up for ball milling

The steel/glass balls were selected instead of stone aggregates because they do not absorb water or paste and therefore it would be possible to extract the paste for the flow tests. Glass marbles were selected because the density (2575 kg/m^3) is almost same as that of stone aggregates. Of course, there will be some differences between the effects of the balls and the aggregates, as the size, shape and surface texture of these are different. Cement paste and steel balls/glass marbles were used in the ratio of 1:1 by volume. Different sizes of steel and glass marbles were selected based on the percentage fraction of aggregates (Mehta and Monteiro, 2005); 30% were of 25mm size, 40% were of

17.5mm and 30%, 12.5mm. The paste was mixed by hand for 1 minute before putting it into the drum and then the steel balls /glass marbles and superplasticizer were added and the paste mixed for 4 minutes. The mixing was done by rotating the drum at 32 rpm. The paste was screened through 4.75 mm and 600 micron sieves before the Marsh cone test.

3.4.4. Results and Discussions

Figure 3.13 shows the Marsh cone flow times for the different mixing methods and dosages of superplasticizers. In all cases, there is an increase in fluidity with an increase in the dosage of superplasticizer up to a certain dosage, which is taken as the saturation dosage (Agullo et al., 1999). The saturation superplasticizer dosages in the case of Hobart mixer with B-flat beater and ball milling with steel balls and glass marbles are comparable as seen in Table 3.5. The unit weights of paste prepared are almost same, as shown in Table 3.5, which implies that air entrainment does not vary for different mixing methods. The blender mixing gives a higher fluidity but the saturation dosage is also higher. In addition, the paste prepared with the blender had a temperature that was about 10-12 ºC higher than that prepared with the other methods. The saturation dosages obtained through grinder mixing and Hobart with D wire whip is comparable. Hand mixing gave the lowest fluidity. The results of three trials for selection of mixing method are given in Table A.1 of Appendix A.

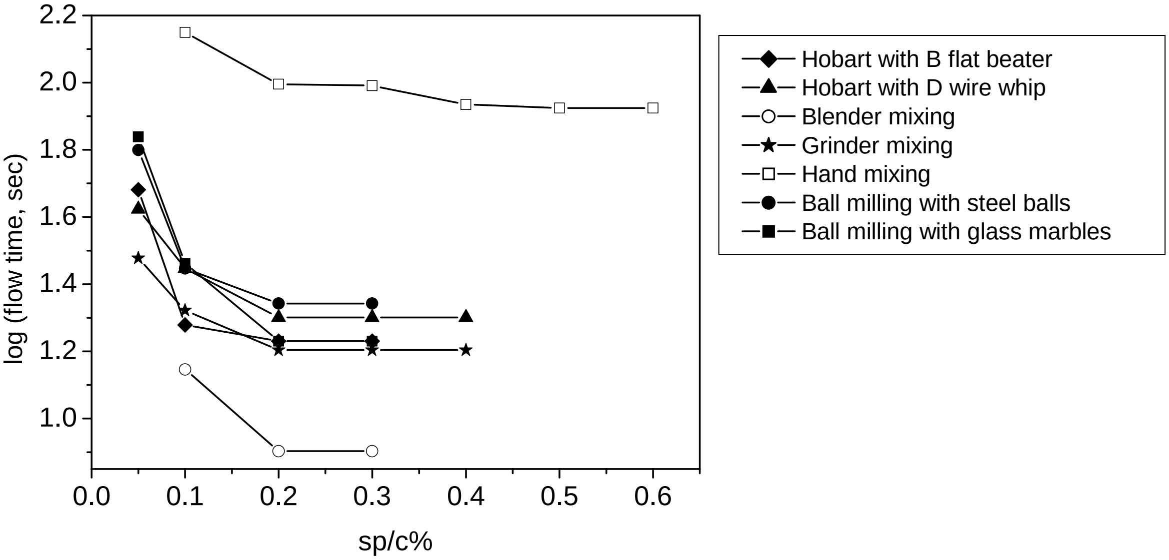


Fig. 3.13 Typical flow time curves obtained with Marsh cone for different mixing methods

Table 3.5 Optimum superplasticizer dosage and range of unit weight for different mixing methods

Type of mixing	Saturation superplasticizer dosage %	Unit weight of paste (kg/ litre)
Hobart with B flat beater	0.09	1.97-2.03
Hobart with D wire whip	0.16	1.97-1.99
Blender mixing	0.16	1.94-2.02
Grinder mixing	0.16	1.97-2.05
Hand mixing	0.20	1.93-1.95
Ball mill effect (steel balls)	0.11	1.96-2.00
Ball mill effect (glass marbles)	0.14	1.94-1.98

The mini-slump spread generally increases with an increase in the dosage of superplasticizer, as shown in Figure 3.14. The points that have been omitted in the figure correspond to higher dosages where there is bleeding. Generally, it is seen that bleeding occurs when the dosage is well above the saturation dosage and the tendency for it to occur increases with the intensity of the mixing.

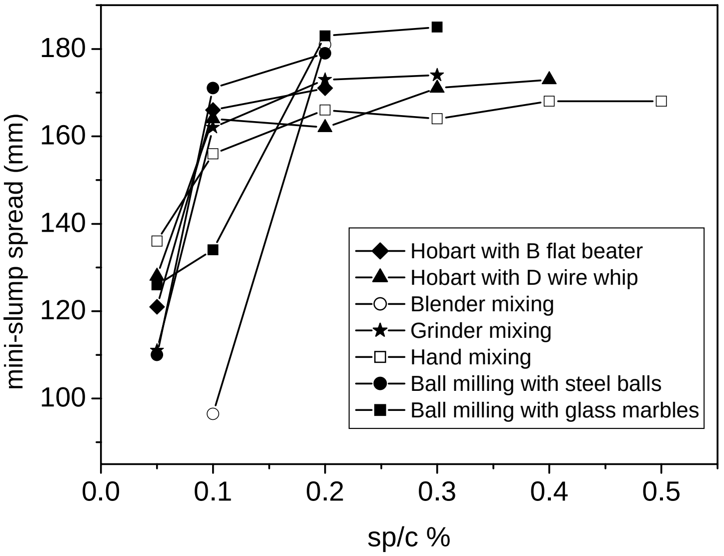


Fig.3.14. Typical flow curves obtained with mini-slump for different mixing methods

Considering the different types of mixing studied here, it can be stated that the blender, Hobart mixer with the flat beater and ball mill provide intensive mixing, with the blender being the most intensive of the three while the hand mixing, grinder and whip mixing are not intensive. In the case of intensive mixing, the mixing is expected to yield better dispersion of the particles and the breaking up of the initial hydration products (e.g., first growth of ettringite). The higher mixing intensity also appears to decrease the superplasticizer demand, in terms of the saturation dosage, with the exception of the blender, which results in a higher saturation point probably due to the higher surface area of the particles due to the crushing of the hydration products. The effect of a high dosage of superplasticizer is also more evident in the case of intensive mixing with bleeding occurring beyond the saturation point. The values of the unit weight (Table 3.5) of the paste from different mixing methods show that the variation for different dosages is small. This shows that there is not much segregation of paste for different mixing methods.

In a concrete mixer, it is expected that the cement paste is mixed in an intensive manner. This was simulated, to a large extent, by the ball mill. Since the behaviour of the paste mixed with the Hobart mixer with B-flat beater and the ball mill is similar in terms of saturation dosage and fluidity, it can be concluded that the Hobart mixer leads to a paste that is representative of that in concrete.

3.4.5 CONCLUSIONS

- The Marsh cone and mini-slump tests are suitable methods for the objective comparison of the effects of different mixing methods on the fluidity of superplasticized cement pastes. Both are simple methods to determine the comparative fluid behaviour and saturation superplasticizer dosage.
- The mixing with Hobart mixer with a flat beater and a ball mill with glass/metal can be categorized as intensive as in concrete mixing.
- In the case of blender mixing, the mixing is more intensive, leading to a higher saturation dosage of superplasticizer and more fluidity. The temperature rise of the paste prepared with this mixing method is 10-12 ºC higher than that with other methods and causes rapid hydration leading to change in microstructure.
- The results presented indicate that the paste prepared with the Hobart mixer with flat beater can be considered as representative of the paste of concrete since the properties are similar to that of paste mixed in a ball mill, with steel/glass balls, in terms of saturation dosage as well as flowability. Hence, pastes will be prepared using the Hobart mixer with flat beater for the rest of work in this thesis.

3.5. INFLUENCE OF TYPE AND DOSAGE OF SUPERPLASTICIZER ON THE FLOW BEHAVIOUR OF CEMENT PASTE

In the previous section, Marsh cone and mini-slump tests were used to study the fluidity of cement paste and for selecting a suitable mixing method for the preparation of cement paste. These are simple empirical methods to characterize flow behaviour of cement paste whereas rheological tests are fundamental but more complicated and require skill for conducting the tests. Hence, the establishment of correlations between these tests helps to select an appropriate test to study the fluidity of cement paste and to understand the results from empirical tests better. This study is more relevant considering incompatibility problems associated with superplasticized cement paste (see Chapter 2), which necessitate the use of simple tests for studying different combinations of cement and admixture. As the admixtures mainly affect the flow behaviour of the cement paste without significant interaction with the aggregate, it seems reasonable to select admixtures and evaluate their performance through tests on the cement paste.

3.5.1 Testing Details

In the previous section, it was concluded that cement paste prepared with the Hobart mixer and B flat beater represents that of concrete satisfactorily. Hence, the same mixing method, with the exception that the superplasticizer addition was delayed further to two minutes after the mixing of cement and water to get better efficiency. All the material components were kept in a humidity chamber at a temperature of 27°C for one day before the tests in order to minimize the effect of ambient temperature on the flow behaviour. Marsh cone, mini-slump and viscometer tests were done as explained in Section 3.3

3.5.2 Results and discussions

The Marsh cone flow time curves for different types and dosages of superplasticizers are shown in Figure 3.15, along with the saturation dosages corresponding to the internal angle of 140°± 10° for each case (following the method of Gomes et al., 2001); the individual data are given in Table 3.6. The results show that fluidity increases with an increase in the dosage of superplasticizer up to the saturation point, after which the curves remain relatively flat.

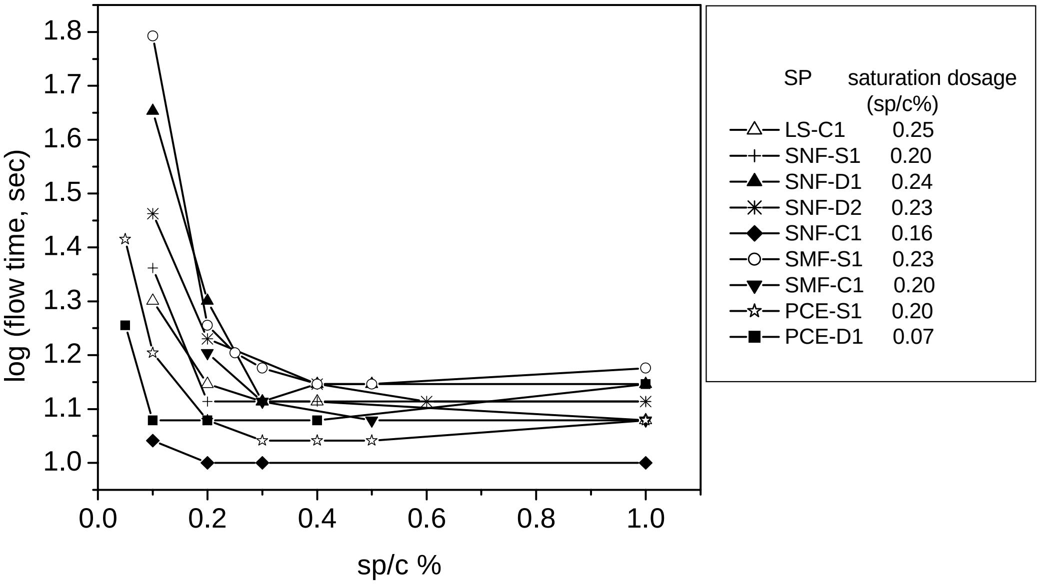


Fig. 3.15 Marsh cone flow time for different superplasticizers

The lignosulphonate-based product LS-C1, though not expected to be as effective as the other products, yields a response that is similar to those of the naphthalenes and melamines. Most of the admixtures based on naphthalenes and melamines exhibit similar flow time curves, except for SNF-C1, which yields lower flow times and a comparatively low saturation superplasticizer dosage of 0.16%. In comparison, the PCE-based superplasticizers are more effective, with lower saturation dosages than the other products; PCE-D1 gives the lowest saturation dosage of 0.07%. These trends are in accordance with the basic actions of the different families of superplasticizers (see Chapter 2).

The mini-slump test results (see Figure 3.16) show that the spread increases with the increase in dosage of superplasticizer. However, bleeding was observed in the paste whenever the saturation superplasticizer dosage was exceeded. The mini-slump spread (i.e., flow) is least for SNF-D2 and highest for PCE-D1. The time taken for a spread of 115 mm at saturation dosage is less than 1 sec.

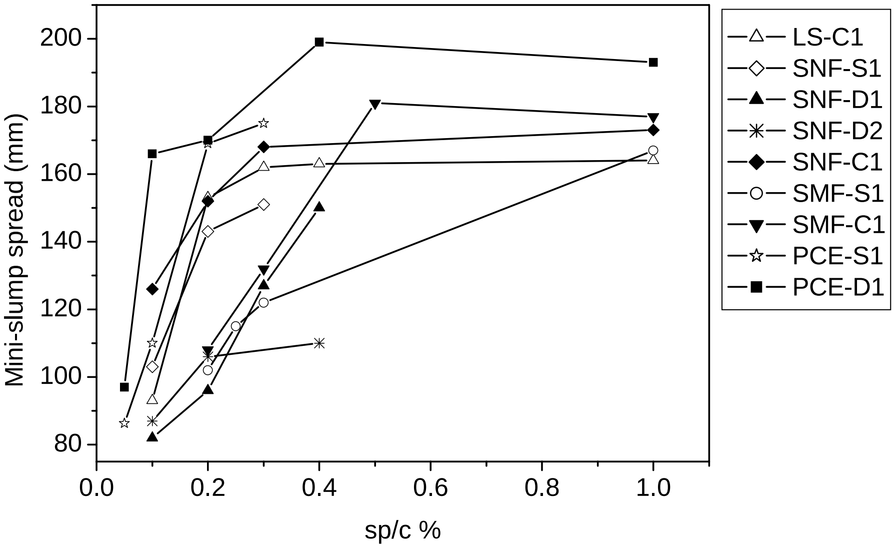


Fig. 3.16 Mini-slump spread for different superplasticizers

In Figure 3.17 Marsh cone and mini-slump spread are plotted together, showing that as the flow time increases, the mini-slump spread decreases. A better correlation is observed for pastes with high fluidity.

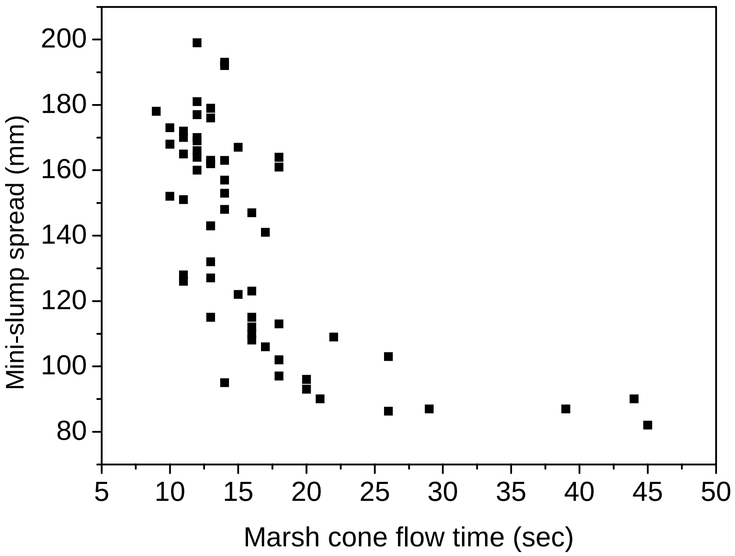
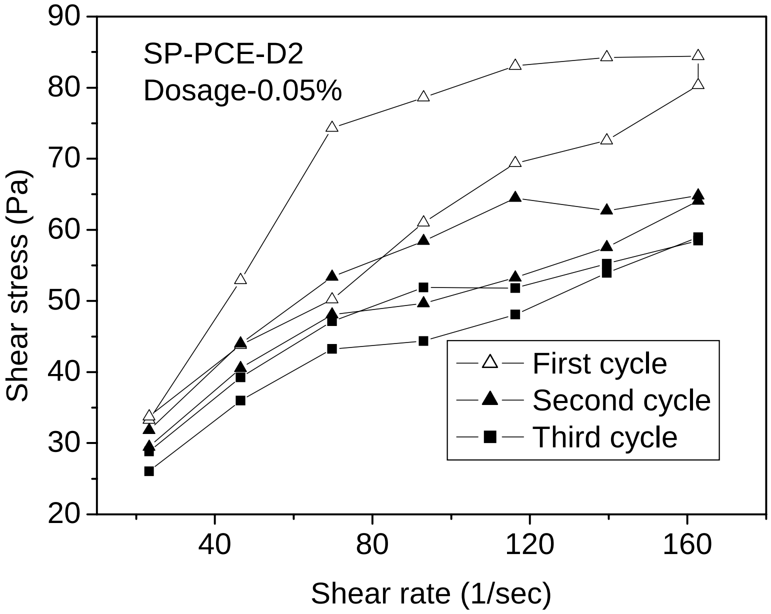
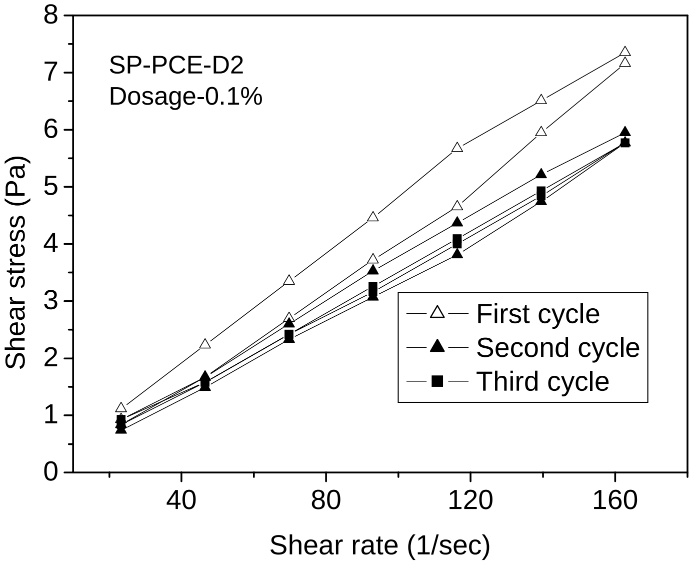


Fig. 3.17 Correlation between Marsh cone flow time and mini-slump spread

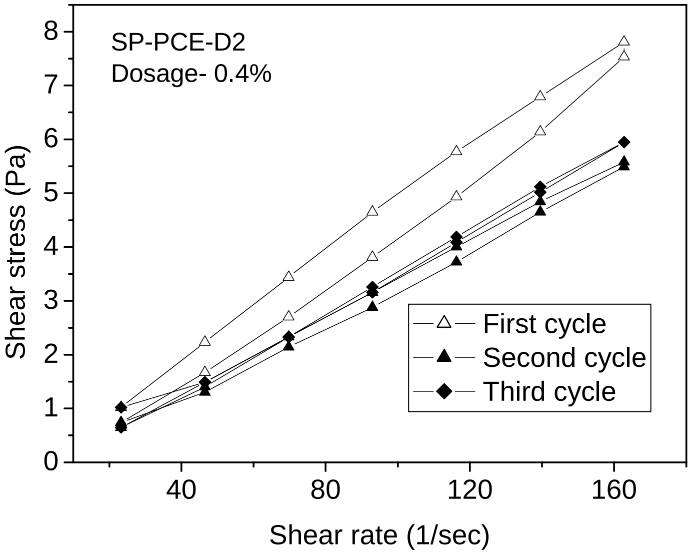
A typical set of shear stress-strain rate curves obtained from the rheological tests are shown in Figure 3.18 (a-c) for pastes with the superplasticizer PCE-D1. At the low dosage of sp/c = 0.05%, the area within the loading-unloading loop of first cycle is much higher than the subsequent cycles, reflecting the energy needed for the structural breakdown of the paste (see Figure 3.18 a). Moreover, it can be seen that the curves are nonlinear reflecting the shear-thinning response. At the sp/c dosage of 0.1%, which is just above the saturation dosage, the shear stress levels are remarkably lower, as seen in Figure 3.18 b, and the stress-strain rate response is practically linear, especially in the second and third cycles. At both dosages (see Figures 3.18 a&b), it is observed that the areas within the loading-unloading loop decrease, along with the stress levels, in subsequent cycles. At the higher superplasticizer dosage of 0.4% (see Figure 3.18 c), the curves are similar to that of sp/c = 0.1% but with two significant differences; i.e., the response of the third cycle is above that of the second cycle and the response in the third cycle shows slight shear-thickening behaviour, indicated by a slight increase in the slope of the stress-strain rate curve. These two aspects can be attributed to the settlement of the cement particles due to the over dosage of the superplasticizer leading to the stiffening of the lower part of the paste, as observed visually in this work and in previous works (Bhatty and Banfill, 1982; Billberg, 1997; Cyr et al., 2000; Papo and Piani, 2004). At higher strain rates, more of the settled flocs of cement particles are forced into the suspension, which would increase the stress resulting in the strain-hardening effect. Responses similar to those presented in Figures 3.17 a-c were observed for all the admixtures, except that no shear thickening could be seen for LS-C1 and SNF-C1 even at the dosage of 1%.



(a) Hysteresis cycles at low dosage



(b) Hysteresis cycles at optimum dosage



(b) Hysteresis cycles at excess dosage

Fig. 3.18 Typical graphs showing three hysteresis cycles for a PCE based superplasticized cement paste at (a) low (b) optimum and (c) excess dosages

The shear stress-strain data were fitted in each case with the Bingham and Herschel-Bulkley models, and the parameters obtained are given in Table 3.6. It can be observed that, in general, an increase in the dosage of superplasticizer reduces the yield stress and plastic viscosity of the Bingham model, which is attributed to the better dispersion of cement particles (Rixom and Mailvaganam, 1999). The Bingham yield stress tends to reduce to zero, as the superplasticizer dosage increases; the drop in yield stress is sharpest in the case of the PCE-based products, confirming the results of previous works (Puertas et al., 2005). The plastic viscosity decreases initially with an increase in the dosage of superplasticizer but remains practically constant after a certain point. In the case of the Herschel-Bulkley model, the yield stress (τ_0) has the same trend as that of the Bingham model though the values of the former are lower at smaller superplasticizer dosages and vice versa at higher dosages. These differences are attributed to the change in the rheological nature of the paste from shear-thinning to slight shear-thickening, as discussed earlier. The consistency and power index (n) of the Herschel-Bulkley model are interdependent and hence well defined trends could not be identified for the individual parameters. Note that for shear-thinning materials, $n < 1$, and that for shear-thickening materials, $n > 1$.

Table 3.6 Rheological characteristics and Marsh cone flow times

Type of sp	sp/c %	Experimental flow time (sec)	Bingham Parameters		Herschel Bulkley Parameters			Flow time predicted by the Nguyen et al. approach	
			τ_0 (Pa)	μ_p (Pa S)	τ_0 (Pa)	K (Pa S^n)	n	Bing-ham material (sec)	Herschel Bulk-ley (sec)
LS-C1	0.1	20	12.2	0.122	11.0	0.319	0.817	18	16
	0.2	14	5.8	0.089	5.0	0.169	0.880	14	13
	0.3	13	2.0	0.059	2.0	0.053	1.017	12	12
	0.4	13	1.0	0.050	0.7	0.077	0.920	11	10
	1	12	0.5	0.068	0	0.135	0.876	12	11
SNF-S1	0.2	13	16.2	0.143	12.29	0.668	0.723	20	16
	0.3	11	1.8	0.055	1.66	0.066	0.965	11	11
	0.4	11	0.0	0.033	0.08	0.030	1.020	10	10
	1	11	0.1	0.031	0.12	0.029	1.010	10	9
SNF-D1	0.1	45	18.31	0.197	14.34	0.657	0.783	27	22
	0.2	20	12.13	0.139	11.69	0.265	0.872	20	17
	0.3	13	2.88	0.074	3.09	0.059	1.041	13	13
	0.4	14	0.08	0.049	0.18	0.043	1.027	11	11
	0.5	14	0.11	0.043	0.47	0.021	1.132	11	11
	1	14	0.09	0.033	0.45	0.013	1.177	10	11
SNF-D2	0.1	29	16.99	0.197	20.46	0.034	1.328	27	30
	0.2	17	6.94	0.088	7.56	0.100	0.959	14	14
	0.4	14	0.55	0.042	0.98	0.017	1.168	11	12
	0.6	13	0.37	0.041	0.67	0.022	1.113	11	11
	1	13	0.13	0.045	0.29	0.034	1.049	11	11
SNF-C1	0.1	11	6.72	0.057	5.12	0.269	0.722	12	10
	0.2	10	1.25	0.042	1.95	0.008	1.300	10	12
	0.3	10	0.72	0.029	1.20	0.006	1.303	9	11
	1	10	0.24	0.023	0	0.050	0.876	9	8
SMF-S1	0.1	62	20.39	0.177	3.24	4.914	0.43	26	16
	0.2	18	6.89	0.076	6.33	0.103	0.948	14	14
	0.25	16	2.36	0.098	1.99	0.128	0.950	15	14
	0.3	15	1.54	0.078	1.34	0.109	0.950	13	13
	1	15	0.77	0.048	0.98	0.033	1.06	11	11
SMF-C1	0.1	>120	33.14	0.199	20.53	2.514	0.559	36	24
	0.2	16	13.44	0.128	6.36	1.07	0.638	19	14
	0.3	13	2.88	0.074	3.09	0.059	1.040	13	13
	0.5	12	0	0.039	0.08	0.025	1.090	10	11
	1	12	0	0.037	0.13	0.020	1.115	10	11
PCE-S1	0.05	26	17.55	0.155	15.93	0.310	0.873	23	20
	0.1	16	11.07	0.089	16.01	2.399	0.558	15	20
	0.2	12	0.51	0.073	0.68	0.010	1.260	13	12
	0.3	11	0	0.034	0.44	0.007	1.270	10	11
	1	12	0	0.034	0.39	0.006	1.344	10	12
PCE-D1	0.05	18	24.45	0.214	1.65	6.910	0.410	32	19
	0.1	12	0.01	0.035	0.37	0.014	1.168	10	11
	0.2	12	0	0.035	0.48	0.006	1.304	10	11
	0.4	12	0	0.036	0.53	0.006	1.310	10	11
	1	14	0	0.047	0.07	0.020	1.158	10	12

3.5.3 Correlations between the Results from Empirical Tests and the Viscometer

In order to study the relationships between the results from empirical tests (i.e., the Marsh cone and mini-slump tests) and the rheological parameters of cement pastes, the data presented above are compared in this section. It can be seen in Table 3.6 that the Marsh cone flow time increases as the yield stress and plastic viscosity increase. More importantly, the variation of the Marsh cone flow time with the superplasticizer dosage has the same trend as those exhibited by the yield stress and plastic viscosity, as also illustrated in the typical plots of Figure 3.19 (shown for SMF-C1). It can be seen that all three parameters decrease with an increase in superplasticizer dosage until the saturation dosage and remain practically constant after that. Figure 3.19 also shows the trend of the mini-slump spread, where it is seen that the spread increases with the superplasticizer dosage until the saturation dosage, after which it is practically constant. These trends can be generalized to all the paste systems studied in this work, and are in agreement with the results of previous works (Gettu et al., 1997; Monte and Figueiredo, 2003; Schwartzentruber et al., 2006). The correlation between Marsh cone flow time with rheological parameters for other superplasticized pastes are given in Figures A.1 and A.2 of Appendix A.

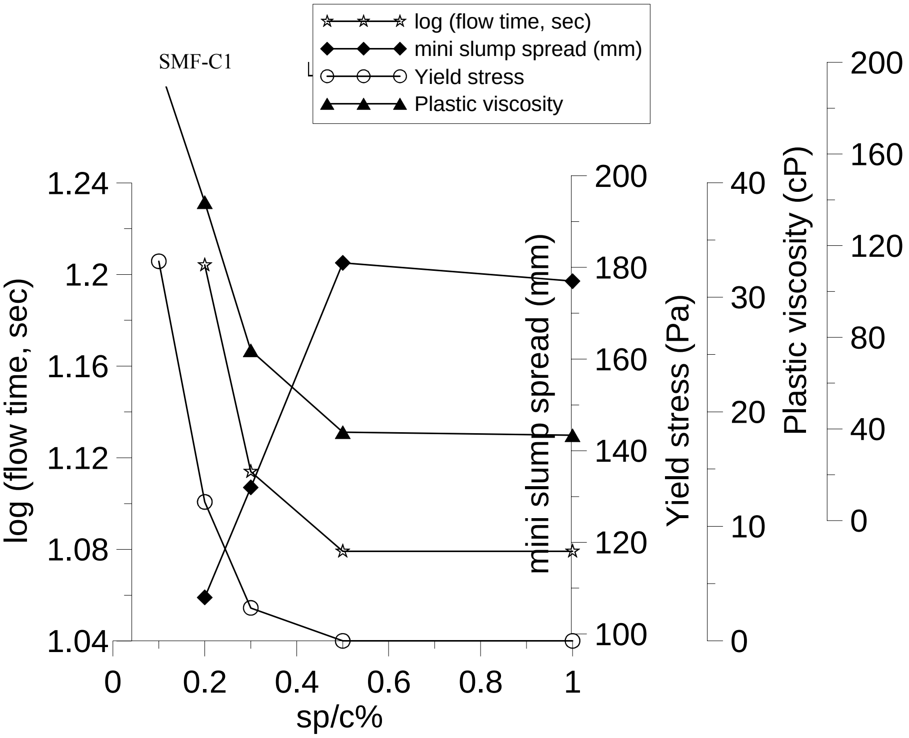


Fig. 3.19 Comparison of data from different tests

The Roussel-Coussot model (Roussel and Coussot, 2005) can be used for estimating the yield stress from the measured conical slump. The model is applicable for different flow regimes based on the height (*H*) and radius (*R*) of the slump cone. According to this model, the spread distance (*R*) can be expressed as a function of the yield stress (τ_c) and material volume (Ω) and density of material (ρ) as expressed in the equation 3.3.

$$\tau_c = \frac{225\,\rho\,g\,\Omega^2}{128\,\pi^2 R^5} \tag{3.3}$$

The prediction of yield stress from mini-slump spread using the Roussel-Coussot model is given in Figure 3.20. The result show that even though the graph shows a good correlation, individual experimental data and predicted values are not comparable.

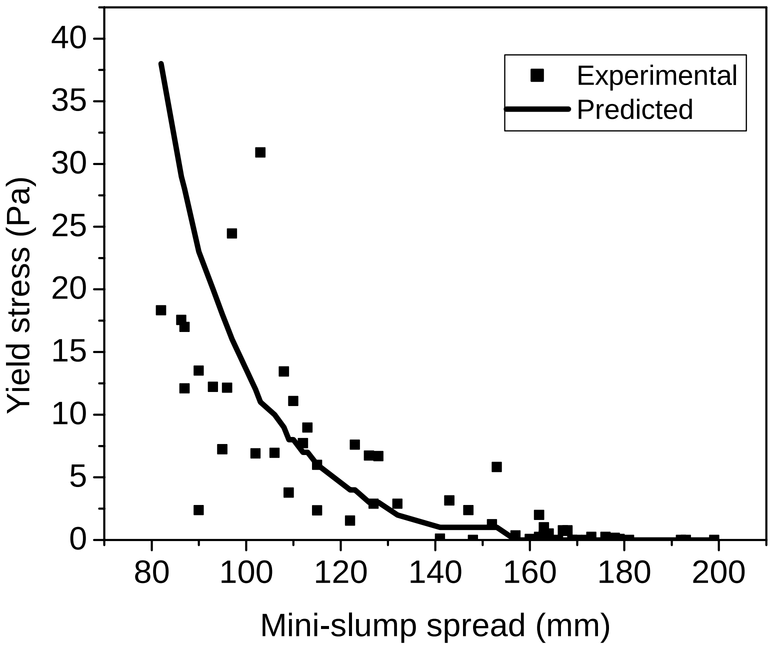


Fig. 3.20 Prediction of yield stress from mini-slump spread using Roussel-Coussot model

It is clear that the saturation dosage estimated with the procedure of Gomes et al. (2001) from the Marsh cone test gives a reliable approximation of the superplasticizer dosage beyond which the plastic viscosity and yield shear stress remain constant. On the other hand, the mini-slump test on the tested pastes does not seem to give as reliable an estimate of the saturation dosage due to bleeding that may occur at higher dosages. From the data obtained, it does not seem possible to identify unique relations between the Marsh cone flow time and mini-slump spread with either the plastic viscosity or yield shear stress, as previously concluded (Ferraris et al., 2001). Nevertheless, it was shown that the use of flow times from two Marsh cones of slightly different geometries can be used to determine the rheological characteristics of a paste (Roussel and Roy, 2005). Conversely, the Marsh cone flow time can be obtained by adequately modeling the flow and material behaviour, as in the semi-analytical approach, where the Marsh cone flow time is obtained from fluid mechanics principles and finite volume method (Nguyen et al., 2006).

Nguyen et al. (2006) suggested a semi analytical approach by for relating rheological parameters to Marsh cone flow time, where it is given that the flow characteristics of cement paste can be described by Herschel-Bulkley model by three parameters τ_0 , k and n which relates the shear stress to shear rate. As per this method, the flow time is related to rheological parameters through the equation 3.4.

$$t = \int_{H_1}^{H_2} \frac{(R + H_t Tan\phi)^2}{\overline{V_\beta}\, R^2} dH_t \tag{3.4}$$

where R is the radius of the nozzle, H_t is height of fluid in the Marsh cone at any time, ϕ is the angle of the Marsh cone, V_β is the corrected velocity at the exit of the nozzle. t is the time taken to lower the level of paste in the Marsh cone from H_1 to H_2.

The flow times for the different pastes studied here have been predicted using this approach considering both the Bingham and Herschel-Bulkley models for the paste and given in Table 3.6. Note that the density of paste was taken as 1.9 kg/litre in the predictions. A Matlab programme was used for solving the equations and for predicting the flow time; the programme code is given in Appendix B.

The results in Table 3.6 show that the predictions of the Nguyen et al. approach are, in general, good for both the rheological models. This confirms that the Marsh cone flow time can be determined through appropriate modeling of the material response and the flow behaviour.

3.5.4 Influence of Type and Dosage of the Superplasticizer on the Non-Newtonian Characteristics of Cement Paste

The non-Newtonian characteristics of the superplasticized cement paste depend on the type of superplasticizer and its dosage and generally rheological model parameters are used to represent the same, as explained in the previous Sections. However, they do not represent the transition in the fluid nature based on the dosage of the superplasticizer. Therefore, steady shear, creep and recovery, and stress relaxation tests were also conducted in order to develop an understanding of the transition of the behaviour of these mixtures from viscoelastic to non-Newtonian to linearly viscous, as the superplasticizer dosage is increased. The test results show that as the superplasticizer dosage increases, in general, there is a transition in the behaviour from viscoelastic to viscous fluid behaviour. It was found that the dosages determined based on the Marsh cone tests were close to the dosages at the transition to the linearly viscous behaviour. The experimental details and the test results are given in detail in Appendix C.

3.5.5 Change of Flow behaviour with Time

The flow properties of cement paste, especially that of superplasticized cement paste, can change significantly after mixing. This is attributed to hydration, intercalation of superplasticizers, chemical degradation of the polymer due to the high pH of the aqueous solution and physical relaxation or change in molecular structure due to adsorption (Tattersall and Banfill, 1983; Justnes et al., 2003). In general, both yield stress and plastic viscosity tend to increase with time (Roy and Asaga, 1980). Consequently, the Marsh cone flow time tends to increase with time (Agullo et al., 1999) whereas the mini-slump spread decreases (Kantro, 1980; Lim et al., 1999).

The change in paste flow behaviour has been studied here by comparing the test results obtained for the same materials just after mixing and 60 minutes later. During the interim period the paste was maintained in an air-tight container at 27ºC. The paste was taken out of the container and mixed for 15 seconds before performing the 60-minute tests. The variation of the flow parameters with time using Bingham model can be seen from the results given in Table 3.7.

Table 3.7 Test data for pastes with different superplasticizers at 0 and 60-minutes

Type of sp	sp/c %	Flow time (sec)		Mini-slump spread (mm)		Yield stress (Pa)		Plastic viscosity (Pa s)	
		0 min	60 min	0 min	60 min	0 min	60 min	0 min	60 min
LS-C1	0.1	20	21	93	90	12.20	13.50	0.122	0.132
	0.2	14	16	153	123	5.81	7.59	0.089	0.097
	0.3	13	13	162	143	2.0	3.15	0.059	0.075
	0.4	13	14	163	163	1.0	0.35	0.050	0.064
	1	12	13	164	162	0.5	0.23	0.068	0.049
SNF-S1	0.2	13	26	143	90	16.21	24.61	0.143	0.185
	0.3	11	11	151	150	1.80	5.91	0.055	0.066
	0.4	11	11	165	163	0.0	0.21	0.033	0.054
	1	11	11	170	178	0.09	0.10	0.031	0.025
SNF-D1	0.1	45	*	82	*	18.31	20.23	0.197	0.241
	0.2	20	70	96	*	12.13	16.61	0.139	0.178
	0.3	13	13	127	115	2.88	5.98	0.074	0.089
	0.4	14	17	bleeding	141	0.08	0.09	0.049	0.083
	0.5	14	18	bleeding	164	0.11	0	0.043	0.045
	1	14	13	bleeding	163	0.09	0.12	0.033	0.035
SNF- D2	0.1	29	*	87	*	16.99	25.52	0.197	0.194
	0.2	17	39	106	87	6.94	12.10	0.088	0.149
	0.4	14	14	bleeding	148	0.55	0	0.042	0.043
	0.6	13	13	bleeding	176	0.37	0.25	0.041	0.039
	1	13	12	bleeding	160	0.13	0.07	0.045	0.038
SNF-C1	0.1	11	14	126	95	6.72	7.24	0.057	0.046
	0.2	10	11	152	128	1.25	6.69	0.042	0.064
	0.3	10	10	168	168	0.72	0.77	0.029	0.046
	1	10	9	173	178	0.24	0.17	0.023	0.035
SMF-S1	0.1	62	*		*	20.39	*	0.177	*
	0.2	18	44	102	90	6.89	2.39	0.076	0.092
	0.25	16	22	115	109	2.36	3.77	0.098	0.101
	0.3	15	18	122	113	1.54	8.97	0.078	0.065
	1	15	18	167	161	0.77	0	0.048	0.043

Table 3.7 (Contd..)

SMF-C1	0.1	>120	*	*	*	33.14	*	0.199	*
	0.2	16	26	108	103	13.44	30.92	0.128	0.139
	0.3	13	16	132	112	2.88	7.71	0.074	0.100
	0.5	12	12	181	169	0	0	0.039	0.042
	1	12	11	177	172	0	0	0.037	0.041
PCE-S1	0.05	26	*	86.3	*	17.55	*	0.155	*
	0.1	16	*	110	*	11.07	23.67	0.089	0.162
	0.2	12	14	bleeding	157	0.51	0.36	0.073	0.068
	0.3	11	13	bleeding	179	0	0.08	0.034	
	0.5	11	14	bleeding	192	0	0	*	0.035
	1	12	12	bleeding	bleeding	0		0.034	0.034
PCE-D1	0.05	18	*	97	*	24.45	*	0.214	*
	0.1	12	16	166	147	0.01	2.37	0.035	0.079
	0.2	12	14	170	bleeding	0	0.09	0.035	0.043
	0.4	12	14	199	bleeding	0	0	0.036	0.036
	1	14	16	193	bleeding	0	0	0.047	0.054

* could not be determined

Generally, in all the compositions tested, the rheological parameters increase with time after mixing, with the increase in yield stress being more pronounced than that of the plastic viscosity. Also, the rate of increase is more significant at superplasticizer dosages less than the saturation point. Similarly, when the dosages are low, the Marsh cone flow time increases with age as seen when the 60-minute data are compared with those obtained immediately after mixing (See Figure 3.21).

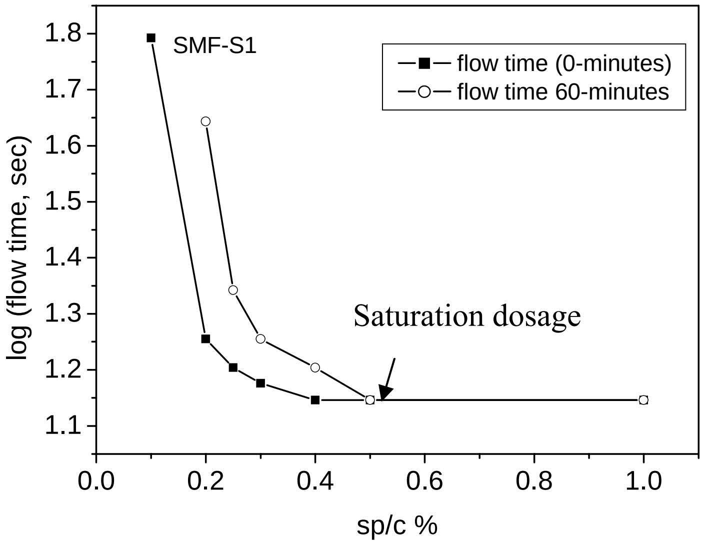


Fig. 3.21 Flow time curve showing the determination of optimum superplasticizer dosage according to Aïtcin, 1998

Note that when the flow behaviour at 60 minutes is more significant (for a particular application) than the immediate behaviour, the saturation point could be defined based on the flow time curves at 60 minutes, or any other critical time (See Table A.2 of Appendix A). Nevertheless, Aïtcin (1998) suggests that the flow time and saturation dosage at 60 minutes should not differ significantly from those obtained immediately for a cement-superplasticizer combination to be considered compatible.

3.5.6 Summary

The following conclusions can be made from the study performed on the flow-related properties of superplasticized cement pastes.

- The flow time determined from Marsh cone test is a good indication of the relative fluidity of superplasticized paste and the saturation dosage obtained from the same test is appropriate for the selection of the superplasticizer.
- Both the Herschel-Bulkley and Bingham models fit the experimental data from the viscometer study satisfactorily. It is observed that the nature of flow in superplasticized paste varies slightly with the dosage of superplasticizer, as follows. At lower dosages, nonlinear shear thinning is generally observed; around the saturation dosage the response follows the Bingham model; and at higher dosages, there may be some shear thickening. The yield stress values obtained with both the models have the same trend with respect to superplasticizer dosage, though the values from the Bingham model tend to be higher at smaller superplasticizer dosages. Even though shear-thickening nature of paste is better represented through the Herschel Bulkley model, the Bingham model represents the behaviour of normal pastes well. The Marsh cone flow times could be

predicted satisfactorily through the Nguyen et al. approach with the parameters of both models.

- An increase in superplasticizer dosage leads to a decrease in the yield stress, plastic viscosity and Marsh cone flow time, and an increase in mini-slump spread, as long as the dosages are below the saturation point. Beyond the saturation dosage, these parameters are practically constant.
- All the nine superplasticizers tested resulted in pastes with good fluidity over 60 minutes when the corresponding saturation dosages were used. It is concluded that the cement-superplasticizer combinations studied here are all compatible as far as the flow behaviour is concerned.

CHAPTER 4

CORRELATIONS BETWEEN THE FRESH AND HARDENED PROPERTIES OF SUPERPLASTICIZED PASTE, MORTAR AND CONCRETE

4.1 GENERAL

Optimization and characterisation of the superplasticized paste is considered as a first step in the design of high performance concrete, as the paste phase is mainly responsible for workability, mechanical properties and durability of concrete. The incorporation of superplasticizers results in the production of high performance concrete due to several beneficial effects associated with it in the fresh and hardened state of concrete. However, the characteristics of cement paste and type and dosage of superplasticizers could sometimes compromise the benefits of incorporating the superplasticizer because of compatibility problems, leading to slump loss, retardation in setting time or excessive heat of hydration (Rixom and Mailvaganam, 1999). Therefore, for the optimization of the composition of high performance concretes (HPC), the optimization of the paste and mortar phases are essential and should include the choice of superplasticizer type and dosage in order to obtain the desired fresh and hardened properties of concrete. The methodology for the determination of the saturation dosage of superplasticizer through the Marsh cone test and its influence on the loss of fluidity has been explained in the third chapter.

Tests involving the paste are simpler and require much less effort than tests of concrete. Nevertheless, results obtained from paste tests need to be correlated to the behaviour of concrete to take the possible influence of aggregates and the aggregate-paste interfaces into account (Ferraris and Gaidis, 1992; Toralles-Carbonari et al., 1996; Roncero et al., 2000; Tang et al., 2001; Giaccio and Zerbino, 2002; Banfill, 2003; Laskar and Talukdar, 2007). For a particular particle size distribution and volumetric fraction of aggregate, the flow properties of concrete are related with rheology of paste, which is generally studied through simple flow or viscometer tests as explained in Chapter 3 (Ferraris and Gaidis, 1992; Toralles-Carbonari et al., 1996; Roncero et al., 2000; Lachemi et al., 2007).

The work presented in this chapter deals with the comparison of the results of tests on superplasticized cement pastes with the behaviour of mortars and concretes. The fluidity of mortar is studied through Marsh cone and flow table spread. Finally, an attempt is made to correlate the cement paste flow behaviour with that of concrete as characterized through the slump, setting time and compressive strength.

4.2 EXPERIMENTAL DETAILS

4.2.1 Materials

The physical and chemical characteristics of cement and four types of superplasticizers used for the correlation study are same as given in Section 3.2. River sand (of 0-4.75 mm grain size range) and crushed granite coarse aggregate (of 4.75-10 mm and 10-20 mm grain size ranges), satisfying the requirements of IS 2386 (2007), are employed in the preparation of concrete.

The sieve analysis was done according to the Indian Standard IS 2386 (2007) and the test results on fine and coarse aggregates are given in Figures 4.1 and 4.2. The sand has a fineness modulus of 2.29 and conforms to grading zone II as per IS 383 (2002). The properties of aggregates are given in Table 4.1. The specific gravity, bulk density and coefficient of water absorption were determined for each aggregate according to IS 2386 (2007). The absorption coefficients for the 10-20 mm, 4.75-10 mm and 0-4.75 mm aggregates are 0.4%, 0.5% and 1.5%, respectively.

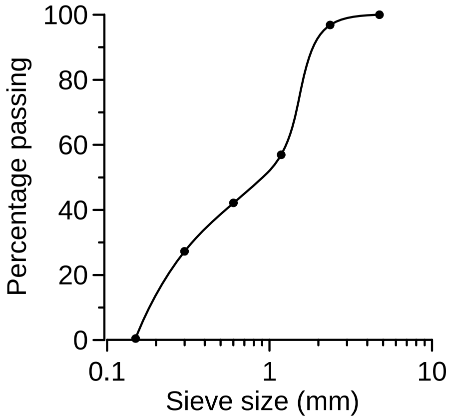


Fig. 4.1 Particle size distribution of fine aggregates (0-4.75 mm)

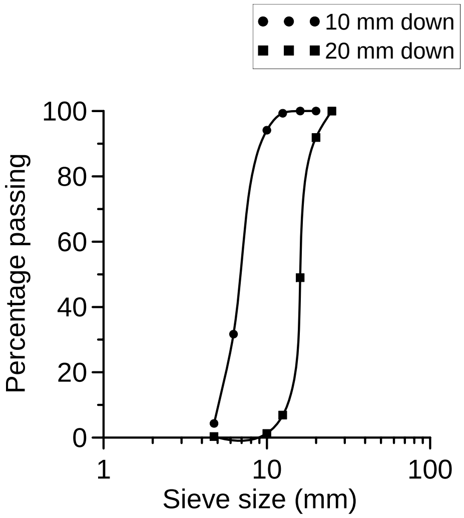


Fig. 4.2 Particle size distribution of coarse aggregates (4.75-20 mm)

Table 4.1 Summary of properties of aggregates

Properties	Sand	Coarse aggregates	
		4.75-10 mm	10-20 mm
Specific gravity	2.62	2.70	2.72
Water absorption (%)	1.5	0.5	0.4
Fineness modulus	2.29	5.71	7.51
Bulk density (kg/ m^3)	1670	1568	1618
Flakiness index (%)	-	-	16.1
Elongation index (%)	-	-	29
Angularity number	-	-	8
Crushing Value (%)	-	-	28
Impact Value (%)	-	-	30

4.2.2 Test Procedures

4.2.2.1 Tests on Paste

The Marsh cone, mini-slump and viscometer tests, as explained in Chapter 3, were conducted for understanding the flow behaviour of the paste. The Marsh cone test results for four superplasticized pastes, already presented in Chapter 3, are summarized in Section 4.3.1.1 for making the comparison of flow behaviours of paste, mortar and concrete possible.

4.2.2.2 Tests on Mortar

Marsh cone and flow table tests (as per IS 1199 (2004) and ASTM C109 (1998)) were used for understanding the fluidity of mortar. A Marsh cone with an aperture diameter of 12.5 mm was used for the mortars. In addition, the consistency of mortars has been determined using a flow table. Here, a hollow truncated metallic cone with a base diameter of 100 mm, top diameter of 70 mm and a height of 50 mm was used. It was placed on the table and filled with mortar, the cone was removed and the mortar was jolted 25 times in 25 seconds causing it to spread. The mean final base diameter was taken as the flow of consistency. In order to account for the higher fluidity of superplasticized cement mortar, the flow table was modified by increasing its diameter using a polycarbonate plate, as shown Figure 4.3. This is in accordance with the test procedure of Domone (2006) for studying the flow behaviour of superplasticized mortars.

Fig. 4.3 Flow table test for mortar

4.2.2.3 Tests on Concrete

In order to correlate the results obtained from paste tests to the behaviour of concrete, tests were conducted on concrete with four superplasticizers studied for paste and mortar. The fresh behaviour of concrete has been characterized using the slump test and the flow table test, as per IS 1199 (2004), as shown in Figure 4.4. For concrete, the following mix proportions were used per m^3: 450 kg cement, 675 kg sand, 454 kg of 20 mm coarse aggregate and 680 kg of 10 mm coarse aggregate with a w/c of 0.35 (mix design as per IS 10262 (2004)). Note that the sand-cement ratio was maintained as 1.5 in both the mortar and concrete. In all the cases, the aggregates were assumed to be in a saturated surface condition and, therefore, the water needed for saturating them was added according to the absorption coefficients given in Table 4.1. The humidity of the aggregates was compensated for, after its determination using the ASTM microwave method (ASTM D 4643 (1987)). The fresh density of concrete with different superplasticizers was also measured to account for the probable air entrainment due to superplasticizers. In addition to the slump and flow table tests, for all superplasticizer dosages, the loss of slump and setting time of concrete at the saturation dosage of superplasticizer were determined. Also, the compressive strengths at 3, 7 and 28 days were evaluated for different dosages of superplasticizers.

(a) Slump test

(b) Flow table test on concrete

Fig. 4.4 Tests for workability of concrete

4.2.3 Mixing Methods for Paste, Mortar and Concrete

The pastes and mortars were prepared in the Hobart mixer (1/6 hp) with the B flat beater at low speed (i.e., shaft speed of 139 rpm and planetary speed of 61 rpm), based on the study explained in Chapter 3. For mixing of the paste, the cement and 70% of the water required were mixed for 2 minutes; after that, the superplasticizer, along with the remaining water (to ensure better dispersion of superplasticizer), was added to the cement paste; the mixing was stopped and the sides of mixer bowl were scraped (for 15-30 seconds); and the paste was again mixed for 3 minutes.

In the case of mortar mixing, oven-dried sand was mixed with the water necessary for its saturation for 30 seconds. Then the cement was added and mixed with the wetted sand for 15 seconds to ensure the homogeneity of solid particles before the incorporation of water. The same sequence as in cement paste was followed for the addition of water and superplasticizer.

For the concrete, the materials were dry mixed and the subsequent mixing sequence for the addition of water and superplasticizer was the same as that for paste; the total mixing time was 5 minutes.

A water-cement ratio (w/c) of 0.35 was employed throughout this study. Also, note that all materials, including distilled water, that were used in the paste and mortar mixes, were kept at a temperature of 27° C in an environmental chamber for at least 24 hours before mixing. This was done to limit the influence of the ambient temperature on the results.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Comparison of the Flow Behaviour of Paste, Mortar and Concrete

4.3.1.1 Flow Behaviour of Paste

Figure 4.5 shows the flow curves for different superplasticized pastes obtained with the Marsh cone immediately after mixing (0 minutes), along with the corresponding saturation dosages; when the flow time is higher, fluidity is less. The saturation dosages and the corresponding flow times are given in Table 4.2. The PCE based superplasticizer performs better than the other superplasticizers in terms of fluidity as well as the saturation dosage (0.07%), as expected. The pastes with low dosages of SMF-S1 exhibit high flow times indicating poorer dispersion of the cement particles at such dosages. Also, at saturation, superplasticizers have different flow times indicating their different effectiveness.

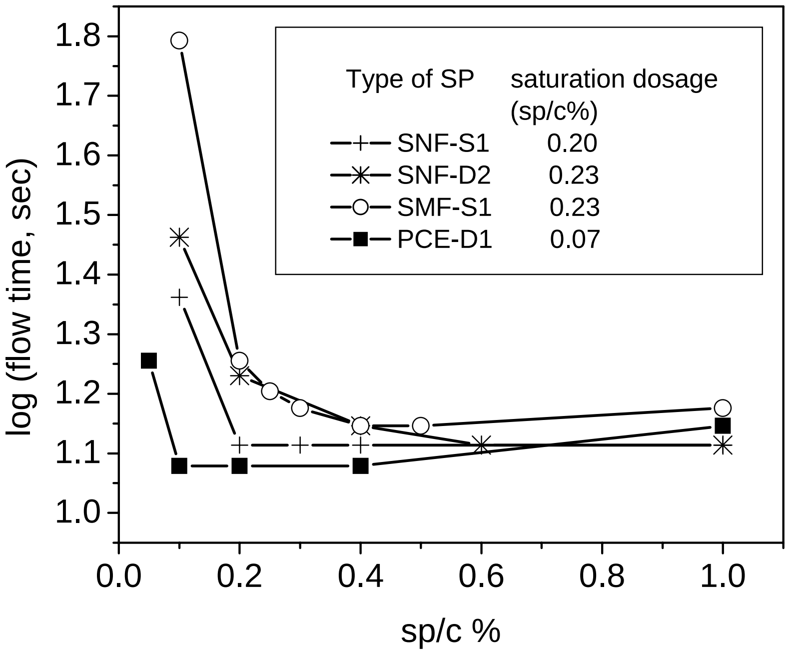


Fig. 4.5 Marsh cone flow time curves for superplasticized cement paste

Table 4.2 Summary of Marsh cone data and concrete cost

Type of sp	Marsh cone test results				*Dosage of sp needed (kg/m^3)	Unit cost/kg (Rs./kg)	*Cost of materials for concrete (Rs./m^3)
	Paste		Mortar				
	Saturation dosage of sp (sp/c%)	Flow time at saturation (sec)	Saturation dosage of sp (sp/c%)	Flow time at saturation (sec)			
SNF-S1	0.20	13	0.22	13	0.23	35	2538
SNF-D2	0.23	17	0.23	22	0.25	50	2570
SMF-S1	0.23	16	0.30	18	0.37	60	2692
PCE-D1	0.07	12	0.07	11	0.08	160	2616

*for a mix with a slump of 100 mm

4.3.1.2 Flow Behaviour of Mortar

The results obtained from Marsh cone test of mortar are shown in Figure 4.6 and in Table 4.2. The fluidity of the PCE based superplasticized cement mortar at low dosages is higher than that with the SNF and SMF based superplasticizers. The PCE yields the highest fluidity with a relatively low saturation dosage whereas the SMF gives the least fluidity and the highest saturation dosage compared to the other products. This is because, even at low dosages, better dispersion is produced due to steric repulsion in the case of the former. Also, it has been observed that high dosages (i.e., above the saturation point) of the SNF with retarder (i.e., SNF-D2) lead to bleeding due to the loss of cohesion in the paste. The flow table test results are given in Figure 4.7, where it can be seen that the spread generally increases with an increase in the dosage of superplasticizer up to the saturation dosage and remains practically constant beyond that; all the mortars exhibited spreads of 250-300 mm at saturation.

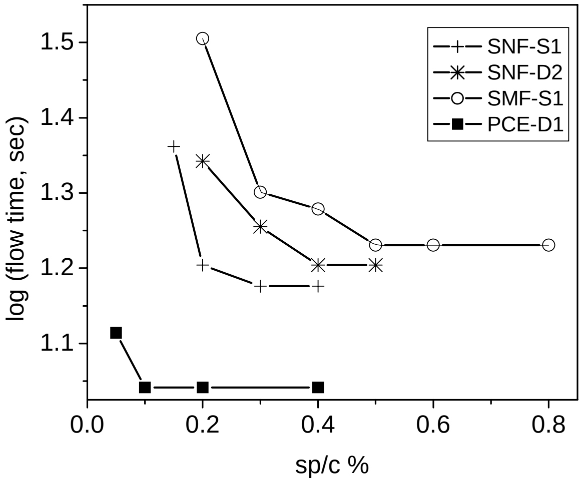


Fig. 4.6 Marsh cone flow times of cement mortar

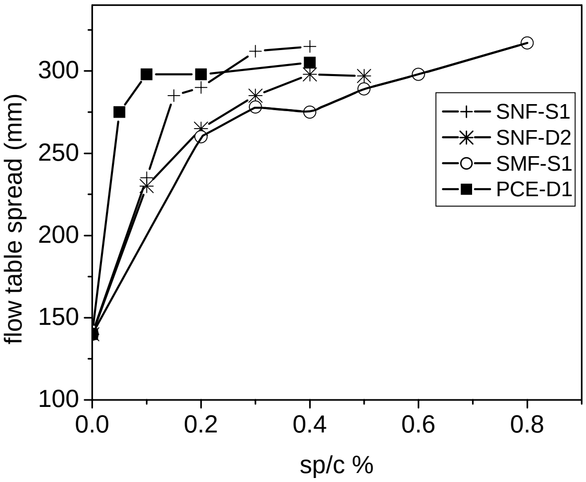


Fig. 4.7 Flow table spreads for superplasticized mortars

Considering that both the flow table spread and the inverse of the Marsh cone flow time are measures of fluidity, it can be seen that the trends obtained in the results with increasing dosage are similar for all the mortars studied. Moreover, the saturation dosages obtained in the mortars are comparable with those obtained from the test results of paste.

4.3.1.3 Flow Behaviour of Concrete

In order to correlate the behaviour of cement paste and mortar to that of concrete and to validate the test of cement paste as a tool for the mix design of high performance concrete, tests were also conducted on concrete with four superplasticizers. The flow behaviour of concrete, with the same paste and mortar compositions as those discussed in the previous sections, has been characterized using the slump and flow table tests as per IS 1199 (2004). The flow table test, which is similar in principle to the flow table test for mortar, was used to measure the flowability of concrete and to observe segregation. Concrete was moulded within the 120 mm high hollow frustum of a cone with bottom and top diameters of 250 mm and 170 mm, respectively. After removing the mould, the spread diameter was measured in four perpendicular directions after jolting for 15 times in 15 seconds. The results of the two tests on fresh concrete are shown in Figures 4.8 and 4.9. The data for all the concretes reflect an increase in slump (see Fig. 4.8) as the superplasticizer dosage increases, as expected. In the case of the naphthalenes, it can be seen that SNF-S1 gives a relatively low slump at its saturation dosage (0.2%) but the slump increases rapidly just beyond this dosage, whereas SNF-D2 gives a steady increase in slump with an increase in dosage though the workability achieved at higher dosages is not as much as with SNF-S1. In comparison, the slump values obtained with SMF-S1 are lower for similar dosages of the other superplasticizers. On the other hand, a fluid concrete with a slump of more than 100 mm is obtained for PCE-D1 even at the dosage of 0.1%.

It can be observed in Figure 4.8 that in order to obtain a slump of 100 mm, the required dosage of superplasticizer is 0.08% for the PCE, about 0.25% for the naphthalenes and 0.37% for the SMF based superplasticizer. The material costs for concretes possessing this slump value have been estimated and are presented in

Table 4.2. The comparison of the costs shows that a low-cost superplasticizer need not always result in cost-effective concrete as the dosage of the superplasticizer for optimum fluidity is also an important factor (Gettu et al., 2006). The results of the flow table spread tests are generally in accordance with those of the slump tests, exhibiting an increase in spread with an increase in the dosage of superplasticizer (see Figure 4.9). Again, the PCE based product performs best and the SMF based product is the least effective.

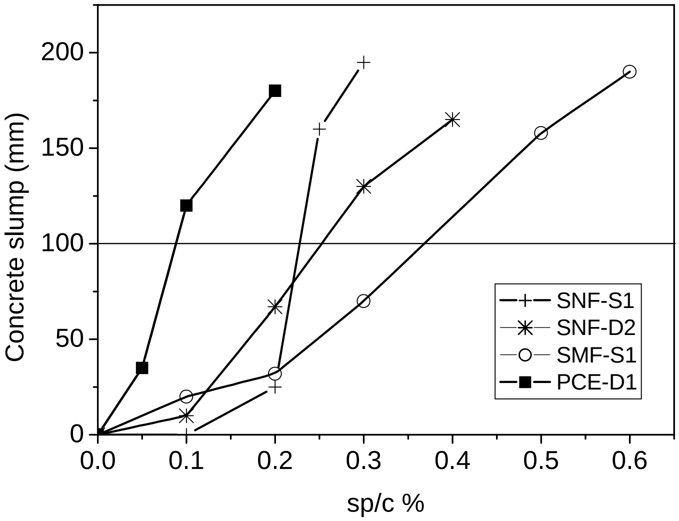


Fig. 4.8 Variation of concrete slump with dosage of superplasticizer

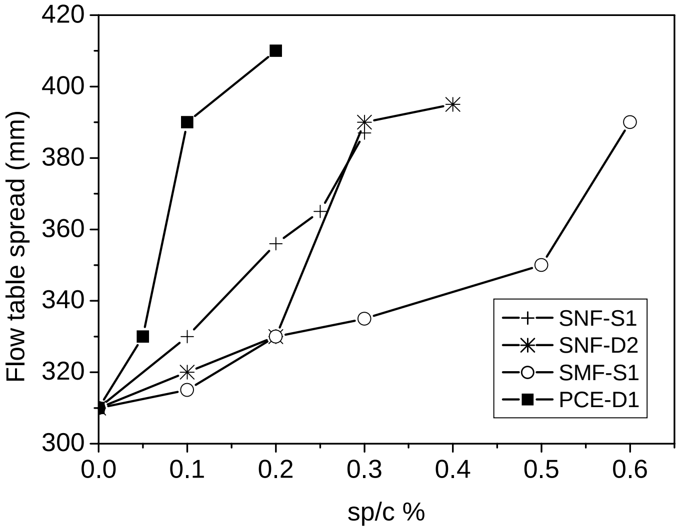


Fig. 4.9 Variation of flow table spread with dosage of superplasticizer

Note that the data from the slump and flow table tests have not been plotted for cases where segregation or bleeding is observed. It is seen that there is a high tendency for segregation and/or bleeding when the superplasticizer dosage is much higher than the saturation dosage, and almost certain to occur when the dosage is close to twice that of saturation. For example, the concrete with a 0.3% dosage of the PCE showed severe bleeding, segregation and stiffening within 5 minutes after mixing. The stiffening seen when the superplasticiser is overdosed could be attributed to shear thickening caused by the excess of superplasticizer in the aqueous phase that could interlock leading to the stiffening (Papo and Piani, 2004). This has also been observed in cement pastes in the present study, especially at high dosages.

4.3.2 Correlation between the Fluidity of Paste, Mortar and Concrete

In Figures 4.10-4.13, the results from the Marsh cone tests of pastes and mortars are plotted along with the slump values of concrete as a function of the superplasticizer dosage. It can be seen that the Marsh cone flow time curves of paste and mortar are generally parallel and the saturation dosages are comparable, as previously observed by other researchers (Roncero et al., 1999; Banfill, 2003; Lachemi et al., 2007). The test results of concrete with SNF-S1 and SMF-S1 indicate a low workability at the saturation dosage of paste obtained from the Marsh cone tests whereas in the cases of SNF-D2 and PCE-D1 the saturation dosages yield medium workability in the concrete. In all the cases, a dosage slightly higher than saturation provides good workability. This can be attributed to the absorption of part of the superplasticizer by the fines in the crushed coarse aggregate This is also confirmed through the adsorption studies; the absorbance of the superplasticized paste with aggregate was higher than that of superplasticized paste (the details of the test is given in Chapter 6). Consequently, the amount of superplasticizer available in the cement paste decreases and maximum dispersion of cement particles is not achieved in the concrete at the same dosage as in the paste tests. Therefore, further addition of superplasticizer is required for high slump values in the concrete. Nevertheless, the saturation dosage obtained from paste studies can be used as a guideline for the selection of superplasticizers and the dosage needed in concrete, especially when the gravel or sand does not have large amounts of fines, where it can be expected that the saturation dosages obtained from the paste tests will yield good workability in the concrete, as reported by Roncero et al. (1999), and Hidalgo et al. (2008).

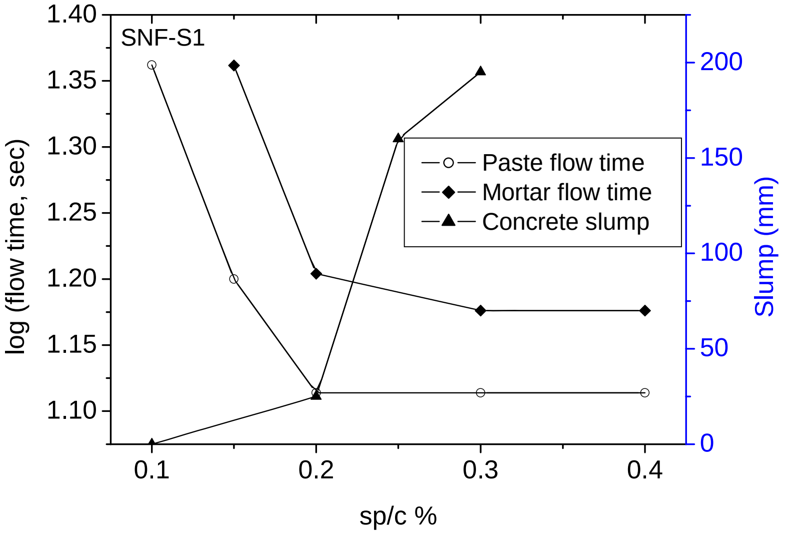


Fig.4.10 Correlation between paste, mortar and concrete in terms of flow time and slump for SNF-S1

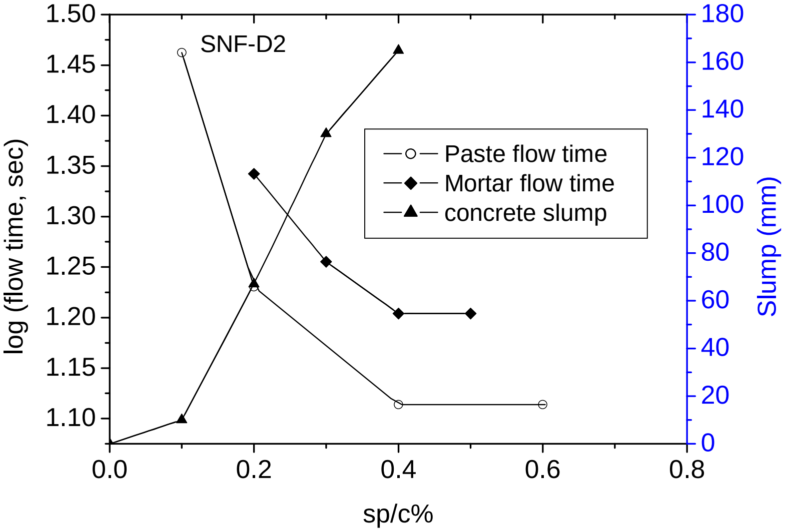


Fig. 4.11 Correlation between paste, mortar and concrete in terms of flow time and slump for SNF-D2

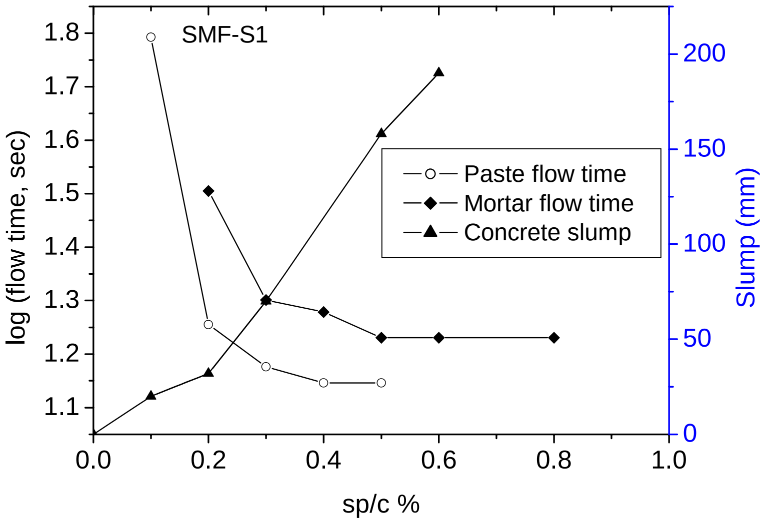


Fig. 4.12 Correlation between paste, mortar and concrete in terms of flow time and slump for SMF-S1

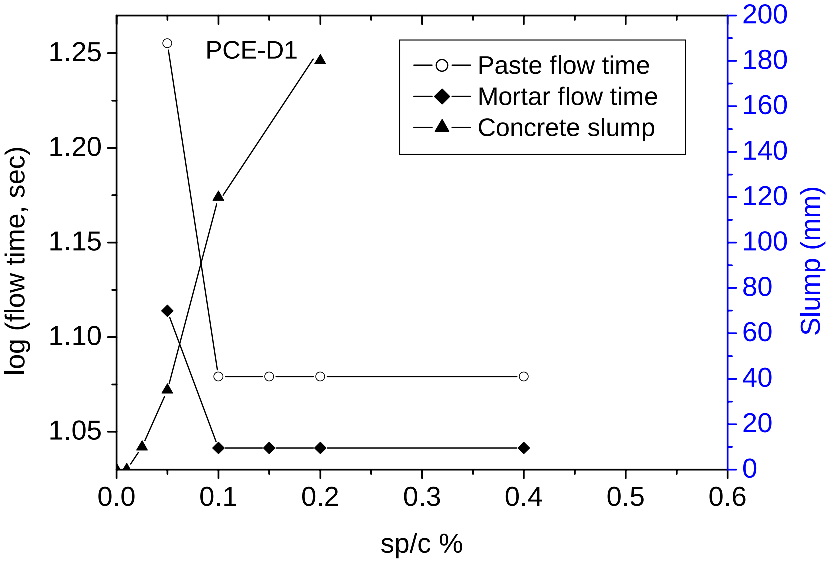


Fig. 4.13 Correlation between paste, mortar and concrete in terms of flow time and slump for PCE-D1

Figure 4.14 shows that no clear correlation exists between the yield stress and plastic viscosity of paste with the slump of concrete. Nevertheless, some observations can be made regarding the data obtained. It appears that a yield stress of less than 5 Pa and plastic viscosity of less than 0.05 Pa s is required to achieve a slump of more than 100 mm. This is in accordance with the reported results of Lachemi et al. (2007), and

Hidalgo et al. (2008). It also appears that the concrete can be categorized as low (<25mm) medium (25-50mm) and high slump (>100 mm) where the values of the yield stress and plastic viscosity of paste have different ranges as indicated in Figure 4.14.

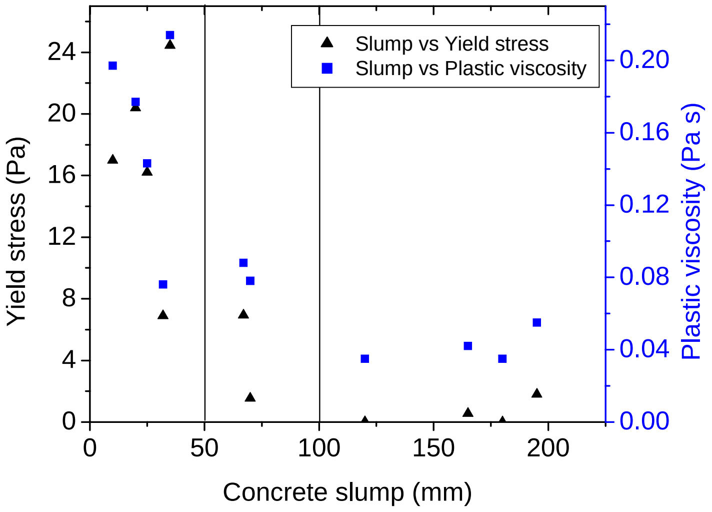


Fig. 4.14 Correlation between slump of concrete, and the yield stress and plastic viscosity of paste

4.4. LOSS OF FLUIDITY

4.4.1. Loss of Fluidity of Paste

The change in the flow behaviour of paste with time has been studied by comparing the results obtained just after mixing and 60 minutes later. During the interim period, the paste was maintained in an air-tight container at 27°C, after which it is taken out of the container and re-mixed for 15 seconds before performing the 60-minute tests.

The Marsh cone flow-time curves obtained after 60 minutes are given in Figure 4.15 (along with the data obtained immediately after mixing plotted with dashed lines for reference). It can be seen that the curves for the 60-minute tests have the same trends as the curves obtained immediately after mixing (denoted hereafter as 0-minute tests), with a decrease in flow time with increase in the superplasticizer dosage upto the saturation dosage, beyond which the flow time does not change much or may even increase slightly (as in the cases of the SMF and PCE based superplasticizers) due to settling of the cement particles in the paste. As before (see Section 3.5.2), it can be observed that the saturation dosages differ with the type of superplasticizer (see values in the inset of the figure).

More importantly, when the 60-minute plots are compared with those obtained at 0 minutes, it can be observed that there is a shift to the right for all the combinations due to higher flow times at 60 minutes, indicating loss of fluidity over this period. The saturation dosage of superplasticizers also increases with time with saturation at 60 minutes occurring at dosages significantly higher than at 0 minutes. This can be attributed to the increase in surface area of the hydrated cement particles and the covering up of the superplasticizer by the newly formed hydrates (see Chapter 2 for further explanations).

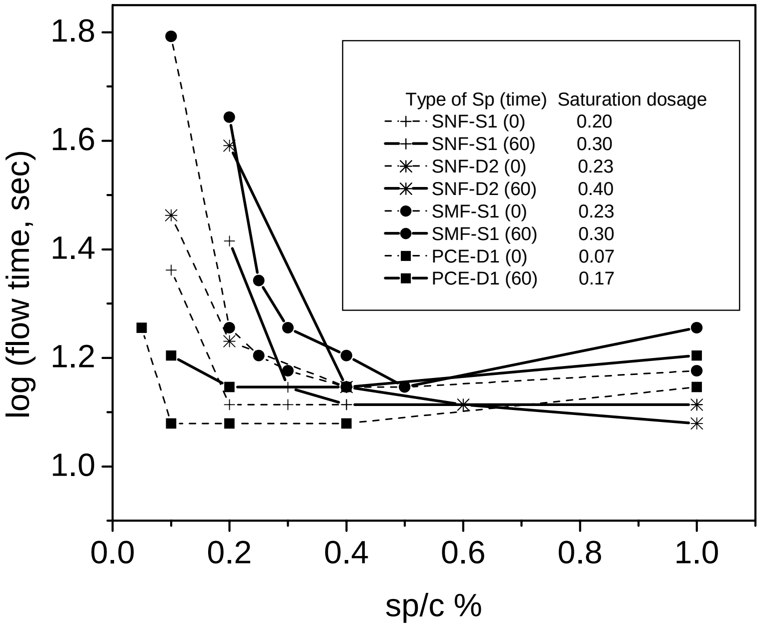


Fig.4.15 Loss of fluidity of paste

The plots in Figure 4.15 also show that the difference in flow time between the 0- and 60-minute curves is higher at lower superplasticizer dosages, with comparable levels of fluidity being achieved at 60 minutes only with initial overdosage of the superplasticizer (i.e., dosage higher than the 0-minute saturation point), except in the case of the PCE, where the 60-minute curve is always above that at 0 minutes. The high fluidity loss at low dosages can be attributed to more rapid flocculation due to inadequate dispersion in pastes with less than saturation dosage. In the context of readymix concrete, the results suggest that when the fluidity of the paste after 60 minutes is more important than the immediate (0-minute) fluidity, the saturation dosage corresponding to 60 minutes should be used in the mix design rather than arbitrarily overdosing the superplasticizer, as is often done in practice.

4.4.2 Loss of Fluidity for Mortar

To evaluate the change in the flow behaviour of mortar with time, tests were conducted with the SMF and PCE based superplasticizers that led to higher loss of fluidity in the paste tests than the others; Marsh cone flow time and flow table spread were measured immediately after mixing and after 60 minutes, and the test results are presented in Table 4.3. It is observed that the flow time increases and the flow table spread decreases with time for both the superplasticizers, especially at lower dosages. The loss of fluidity is higher for the SMF than the PCE, as expected (Chandra and Bjornstrom, 2002b). Note that in some cases the mortar did not pass through the Marsh cone or there were clear signs of bleeding indicating the segregation of the mortar.

Table 4.3 Loss of fluidity of mortar

Type of sp	sp/c %	Marsh cone flow time (sec)		Flow table spread (mm)	
		0	60	0	60
SMF-S1	0.2	22	no flow	242	193
	0.3	21	no flow	265	198
	0.4	13	29	bleeding	260
	0.5	11	15	bleeding	305
	0.8	11	14	bleeding	bleeding
PCE-D1	0.05	13	no flow	310	203
	0.1	11	19	bleeding	281
	0.15	11	15	bleeding	290
	0.2	11	12	bleeding	313
	0.3	11	12	bleeding	315

In the case of SMF based mortar, low dosages of superplasticizers are not sufficient even to initiate the flow after 60 minutes. Moreover, loss of fluidity occurs in the case of the SMF even at the saturation dosage corresponding to the 60-minute tests of pastes whereas for the PCE, there is no appreciable loss at the 60-minute saturation dosage. These results imply that the PCE is more effective in maintaining the fluidity than the SMF, especially at high dosages. However, in both cases the loss of fluidity in the mortar is more than that of the paste.

The results clearly show that when overdosing of the superplasticizer is done to obtain flowable mixes after one hour or so after mixing, the initial mix may segregate. This has to be taken into account during mixing, discharging of the material from the mixer into the truck and transportation. Another important factor is that any material delivered ahead of the estimated delivery time could be segregated and unusable.

The comparison of the paste and mortar test results show that the incorporation of sand does not affect the fluidity or saturation superplasticizer dosage in the 0-minute tests but it seems to increase the loss of fluidity due to the absorption of water and superplasticizer.

4.4.3 Loss of Fluidity of Concrete

To understand the change in flow behaviour of concrete with time, four mixes with the corresponding saturation dosages of superplasticizer (corresponding to 0-minute tests on pastes; see Section 3.5.2) were prepared. The slump was observed at intervals of 30 minutes and the concrete was kept at rest in the pan mixer between measurements; just before each slump test, the concrete was mixed for 15 seconds. The results are shown in Figure 4.16, where it can be observed that the slump decreases with time in all the combinations.

The loss of slump for SNF-S1 is 17% over 30 minutes and 54% over 60 minutes. The loss of slump for SNF-D2 is the least compared to other superplasticizers, as seen in Figure 4.16; it yields the lowest loss in slump of 18% and 26% over 30 and 60 minutes, respectively, reflecting its retarding nature. Slump losses of 54% over 30 minutes and 87% over 60 minutes are obtained in the case of the SMF based superplasticizer, and slump losses of 57 % over 30 minutes and 82% over 60 minutes for the PCE based superplasticizer. The SMF gives a higher loss of slump than the PCE, as already seen in the case of mortar. This loss of slump with time in all cases can be either due to cement hydration or drying due to water evaporation or absorption of superplasticizer and water by the aggregates. The fines in the aggregates also seem to increase the superplasticizer demand over the period of 60 minutes. This indicates that in such cases, the saturation dosage determined at 0 minutes in the paste will not be able to maintain the slump over a long period of time, say 60 minutes, in concrete. When this occurs, it is recommended that the dosage of superplasticizer in the concrete be taken as the saturation dosage obtained in the paste at 60 minutes.

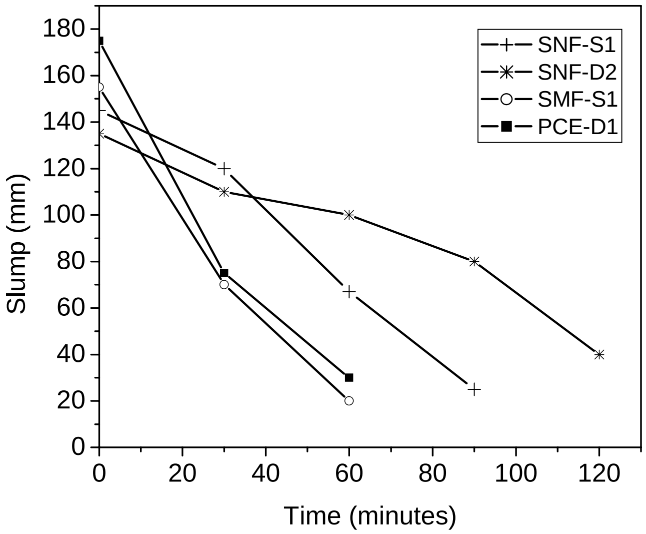


Fig.4.16 Loss in slump of concrete with time

4.5 EFFECT OF SUPERPLASTICIZER ON SETTING OF CEMENT PASTE AND CONCRETE

As already discussed, the superplasticizer slows down the hydration and dissolution of ions, setting of superplasticized cement paste can be retarded (Torrents et al., 1998; Roncero et al., 1999; Brooks et al., 2000). In this study, the Vicat apparatus was used to determine the setting time of superplasticized cement paste. The cement paste was prepared using a Hobart mixer, with a w/c of 0.35 and the saturation dosage of superplasticizer (sp/c%) of each case. In Figure 4.17, the beginning and end of setting (defined as the first incomplete Vicat penetration reading and the first zero penetration reading are shown for each superplasticizer at saturation dosage). The graph shows that retardation produced due to SNF-S1 and PCE-D1 is more than that of the SMF based superplasticizer. This is because the higher molecular weight SMF will be adsorbed more than the lower molecular weight SNF whereas, more of the SNF remains in the solution and retards more than that of SMF. In the case of PCE-D1, the retardation is because of the higher concentration of ionic functional groups (sulphonic and carbonic) in the aqueous phase or due to shorter mean backbone chain lengths in the PCE, in accordance with the reported results of Yamada et al. (2000). The paste with the SNF with the retarder sets more slowly, as expected.

It can be observed that the time difference between the beginning and end of setting varies approximately from 1 to 3 hrs. This shows that for the tested cement paste systems, the superplasticizers lead to a delay in the beginning of setting due to delay in the hydration of alite. However, it does not prolong the setting process because the hydration is not affected further by the superplasticizer, after the beginning of alite hydration (Yamada et al., 2000).

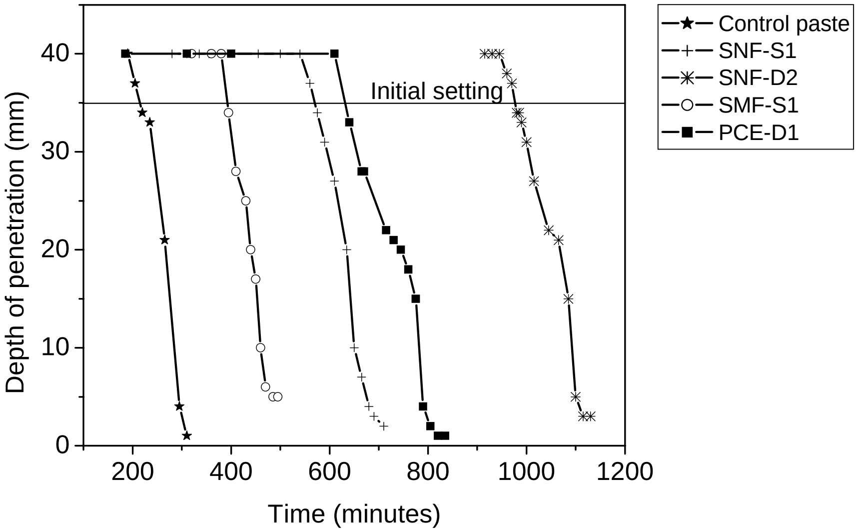


Fig. 4.17 Vicat penetration measurements for pastes with different superplasticizers

The setting time of concrete was determined using a standard penetrometer as per IS 8142 (2002) as shown in Figure 4.18. The concrete was sieved through a 4.75 mm mesh. The passing through mortar was tested, and the results obtained are shown in Figure 4.19. The times at the penetration resistances of 3.43 N/mm^2 and 26.97 N/mm^2 are taken as the initial and final setting times of the concrete, respectively; the setting times of paste and concrete at the saturation dosage of superplasticizer are shown in Table 4.4, along with the paste flow time and slump values. The initial setting time (IST) for the PCE based concrete was 8 hrs and final setting time was 10 hrs. The

SNF-S1 shows a similar trend whereas the SMF sets much earlier and the SNF with retarder (SNF-D2) sets much later. However, except in the case of PCE-D1, the difference between initial and final setting times (FST) is approximately 2 hours in both the paste and concrete. It should be noted that both the Vicat penetration test on paste and the penetration resistance test on mortar measure setting through the determination of the degree of stiffening. Since the initial fluidity of the paste or mortar also affects the stiffness and its evolution, the comparison of the different results is not straightforward, especially since each of the pastes has a different initial consistency. However, it appears that the superplasticizer that causes more retardation of setting in the paste also tends to retard the setting of the concrete having the same paste proportions.

Fig.4.18 Penetration test on concrete; (a) Pocket penetrometer, (b) Penetration test on specimen (c) Impressions made on the surface during measurements

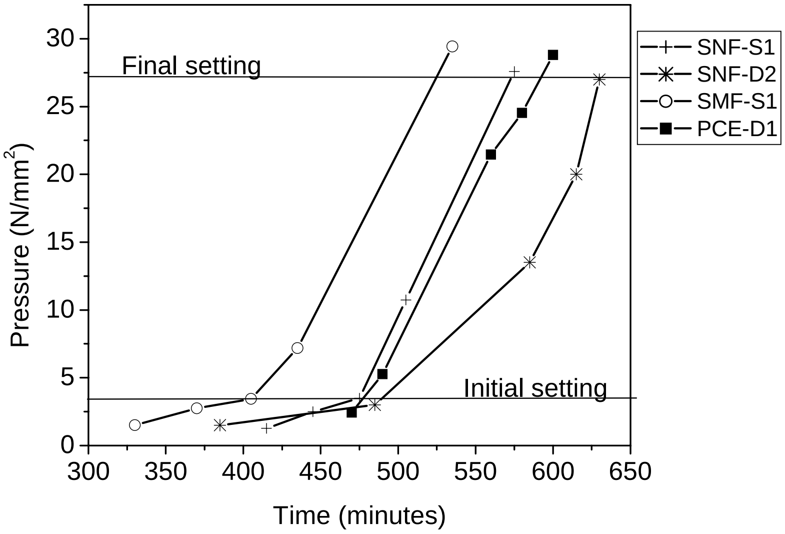


Fig. 4.19 Setting of concrete at saturation dosage of superplasticizer

Table 4.4 Initial and final setting time of paste and concrete

Type of superplasticizer	Paste			Concrete		
	Flow time (sec)	IST (hrs)	FST (hrs)	Slump (mm)	IST (hrs)	FST (hrs)
Control mix	*	3.6	5.2	0	*	*
SNF-S1	13	9.5	11.9	40	7.9	9.6
SNF-D2	17	16.3	18.7	90	8.2	10.5
SMF-S1	16	6.6	8.3	45	6.7	8.8
PCE-D1	12	10.5	14	73	8.0	9.9

4.6 ANALYSIS OF SETTING BEHAVIOUR OF SUPERPLASTICIZED CEMENT PASTE USING ELECTRICAL RESISTIVITY METHOD

4.6.1 Background

The setting of cement paste and concrete is usually determined through penetration resistance, as seen in the previous section. Electrical property measurements are being proposed as an alternative to the penetration measurements for studying the setting and hardening processes within the portland cement pastes over the initial 24 hours of hydration through continuous real time monitoring (McCarter and Curran, 1984; McCarter and Tran, 1996; McCarter et al., 1999, 2003). Calleja (1952a, 1952b) has used electrical resistance measurements for estimating the initial and final setting time of hydraulic materials. Torrents et al. (1998) and Roncero (2000) have used AC impedance spectroscopy over a frequency range of 1 kHz to1 MHz for understanding the influence of superplasticizers on the electrical resistivity of cement paste. More recently, Xiao et al. (2007) have used electrical resistance methods to compare the effect of superplasticizers at the saturation dosage and have correlated resistivity to strength gain and setting time. The previous studies of Srinath (2007) on electrical conductivity of cement mortar at the frequencies of 1, 10 and 100 kHz show that a lower conductivity is obtained at 1 kHz whereas the values are similar at 10 and 100 kHz, indicating that frequencies of 10 kHz and above are adequate for the conductivity measurements on fresh pastes since electrode polarization effects are reduced to negligible proportions (McCarter and Tran, 1996).

The objective of this study is to understand the influence of superplasticizers on the different stages of setting of cement paste based on the electrical conductivity of paste. Tests were conducted with pure cement paste and with 4 types of superplasticizers. The results are compared with standard Vicat test measurements.

4.6.2 Experimental Procedure

Aplab MT 4080A high accuracy LCR meter (hand held AC/DC impedance measurement instrument), which can measure the inductance, capacitance and resistance with imposed currents with frequencies of up to 100 kHz, was used in the present study. A mould with internal dimensions of 50 × 50 × 50 mm was made with polycarbonate plates of 2 mm thickness. This sample size was considered large enough to obtain a representative bulk electrical measurement on paste (following McCarter and Tran, 1996). Stainless steel plates of 50×50 mm were placed on opposite walls of the mould. The cement paste with the saturation dosage of superplasticizer was prepared, as explained in Section 3.4. The sample (cement paste) was placed inside the mould and the steel plates were connected to the H and L ports of the LCR meter to serve as the electrodes (Figure 4.20). Impedance values were determined at the frequency of 10 kHz and the voltage of 1 V_{rms} over a period of 24 hours. The resistance values were converted to electrical resistivity using equation (4.1).

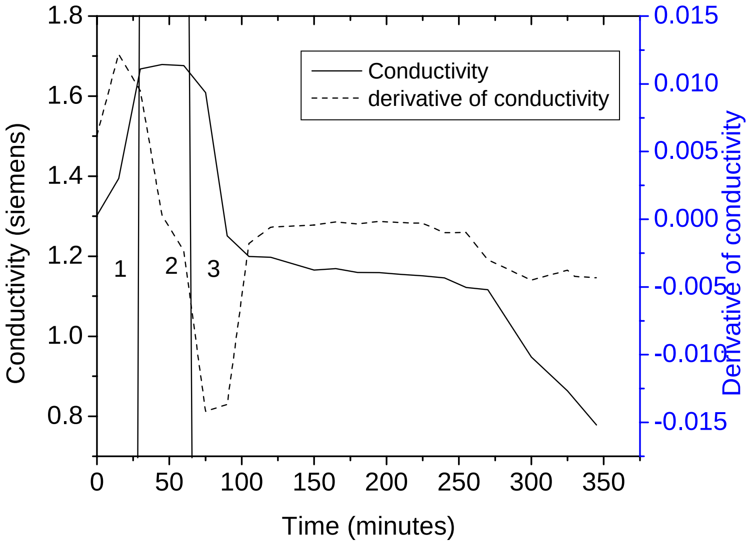
$$\rho = \frac{RA}{d} \text{ ohm metres} \qquad (4.1)$$

where d is the length of the specimen, A is the cross sectional area of specimen, ρ is the electrical resistivity. Due to sample preparation and setting-up procedures, test measurements were taken 15 minutes after mixing. So the zero minute reading presented in the graph in this section corresponds actually to 15 minutes after casting. The resistance values were taken subsequently every 15 minutes over a test period of 24 hours. The top surface of the sample was covered with a polycarbonate plate to avoid evaporation. All tests were carried out in ambient conditions.

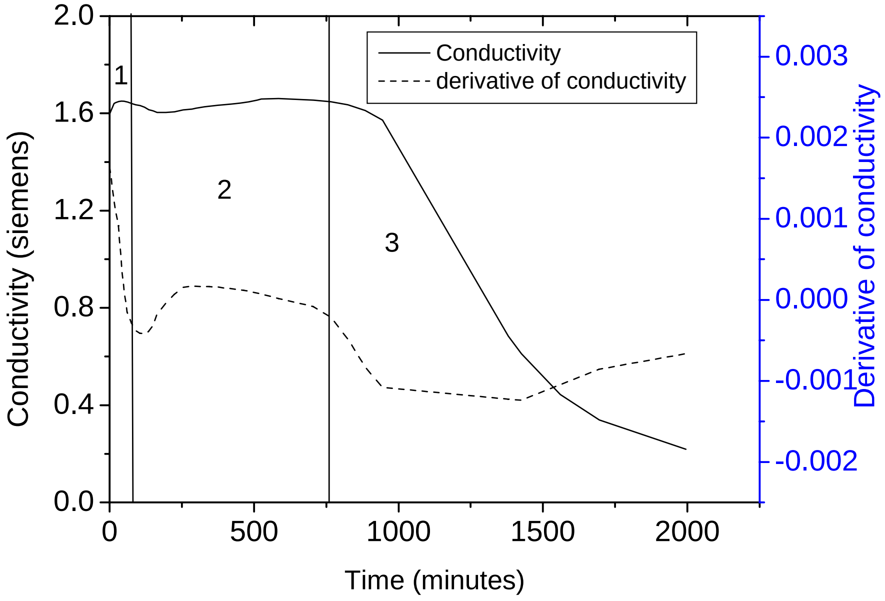
Fig. 4.20 Comparative study on setting behaviour of paste with Vicat apparatus and LCR meter

4.6.3 Results and Discussions

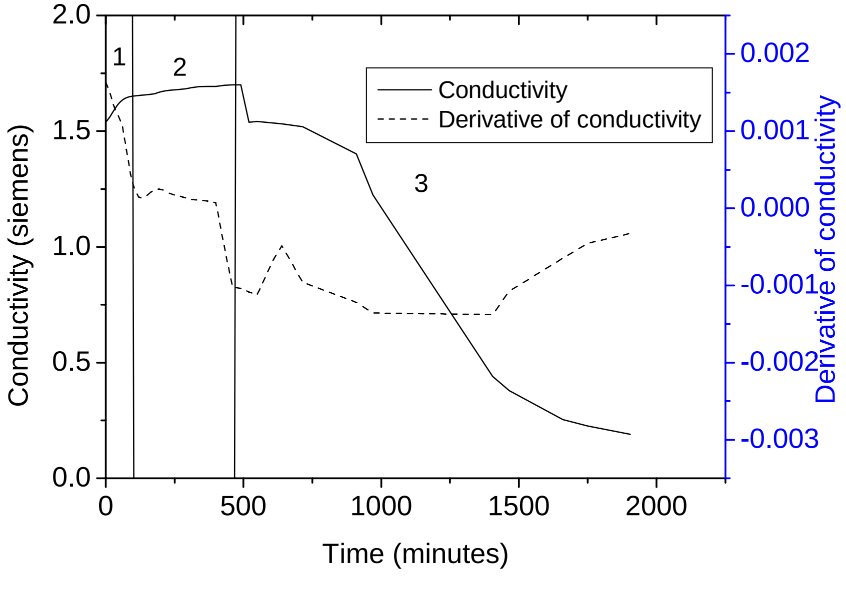
The conductivity and its derivative for pure cement paste and the superplasticized pastes are plotted as a function of time in Figure 4.21. The variation in conductivity can be correlated with the different stages of hydration of cement paste. Stage 1 corresponds to the initial stage in which the conductivity increases due to the dissolution of ions, in all the cases. However, the increase in conductivity is more for the pure cement paste than that of superplasticized pastes. This confirms that the presence of superplasticizer prevents further dissolution of ions, which slows down the increase in conductivity in the initial stage. Stage 2 corresponds to the dormant stage in which the conductivity remains almost constant. In the case of pure cement paste, the dormant stage is caused due to the supersaturation of solution and consequent inhibition of dissolution of ions. The superplasticizer appears to mainly extend this dormant stage and it could be attributed to; (1) the lowering of the rate of chemical reactions further by inhibiting the dissolution of ions due to the presence of superplasticizers in solution; and (2) the formation of an adsorption layer on the cement particle and the formation of complexes with Ca^{2+}. In stage 3, the conductivity decreases as the paste sets and the resistance increases due to the decrease in the mobility of Ca^{2+}, SO_4^{2-} and OH^- ions. The study confirms that the addition of superplasticizer generally extends the dormant stage of hydration process, retarding the onset of acceleration stage, in accordance with the results of earlier studies. (Torrents et al., 1998; Roncero, 2000; Xiao et al., 2007). However, the evolution of the derivative of conductivity clearly reflects the rate of chemical reactions only in the case of pure cement paste.



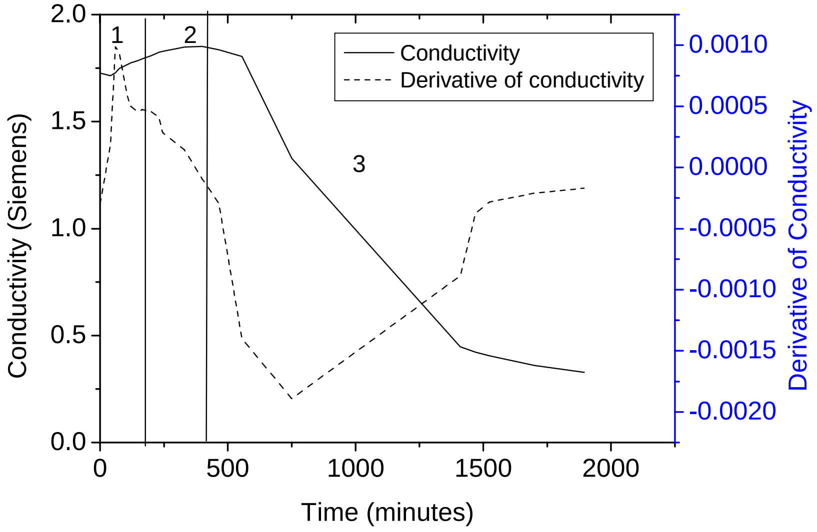
(a) Pure cement paste with w/c = 0.35



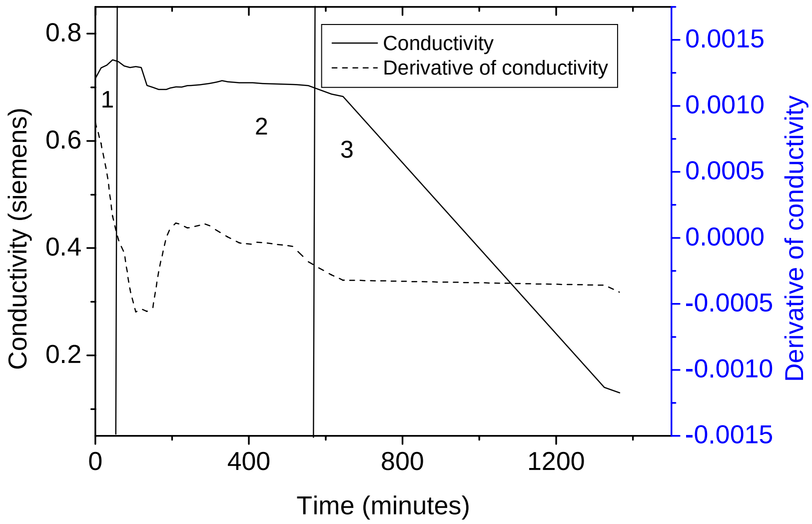
(b) Cement paste with LS-C1



(c) Cement paste with SNF-S1



(d) Cement paste with SMF-S1



(e) Cement paste with PCE-D1

Fig. 4.21 Evolution of conductivity for different superplasticizers

The conductivity curves for the different pastes, along with the beginning and end of setting (IST and FST) obtained from Vicat penetration tests, are shown in Figure 4.22. Compared to pure cement paste, the initial conductivity is much lower for the PCE and similar for the other superplasticizers. As discussed earlier, the results confirm that the dormant stage lasts longer for the superplasticized pastes.

The comparison of the evolution of the conductivity with the Vicat test results shows that for pure cement paste, as well as paste with LS, SNF and PCE based superplasticizers, both the IST and FST fall in the acceleration stage. For the SMF-based superplasticizer, setting begins in the dormant stage whereas the final setting time falls in the acceleration stage. This is in accordance with the penetration test results of both paste and concrete where the retardation of setting was seen to be the least for the SMF-based superplasticizer. It is observed that the superplasticizer that extends the dormant stage of hydration most, yields the highest IST and FST in concrete. Hence, the test results obtained from electrical resistivity method, which is closely related to the chemical activity in the paste, indicate that the setting time is in the following order: Cement paste < Paste with SMF< Paste with SNF< Paste with PCE< Paste with LS.

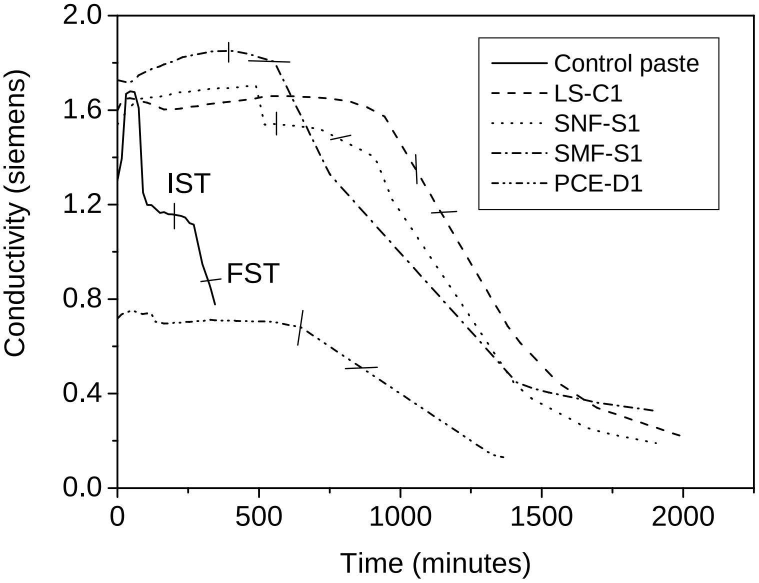


Figure 4.22 Electrical conductivity graphs for different pastes along with beginning and end of setting defined by Vicat penetration measurements

Another point to be noted is that even though the tests are conducted at the saturation dosage for different superplasticizers, the maximum conductivity values varies with the type of superplasticizer. This indicates that the concentration of ions in the aqueous solution is also modified by the type of superplasticizer, especially in the case of PCE-based superplasticizer. This further confirms that the influence of the superplasticizer on setting, as well as on fluidity, varies with its mechanism of action, as explained in Chapter 2. It can be observed from Figure 4.22 that the time difference between the beginning and end of setting is approximately the same in all cases. Hence, it can be concluded that for the present cement paste system, the superplasticizers considered delay the beginning of setting but do not prolong the setting process.

4.7 EFFECT OF SUPERPLASTICIZER ON COMPRESSIVE STRENGTH OF CONCRETE

The compressive strengths of concretes incorporating different types of superplasticizers are shown in Table 4.5. It can be observed that the strength of superplasticized concrete at 28 days is generally more than that of the reference concrete, as also observed by other researchers such as Dhir and Yap (1983), Seung-Bum (1999), Ramachandran (2002) and Kapalko (2006). It can be observed that the concretes with the saturation dosages of the superplasticizer exhibit slightly higher strengths than the reference concrete, probably due to better compaction. Nevertheless, superplasticizer dosages much above saturation lead to bleeding and immediate stiffening, which cause strength reduction.

Table 4.5 Compressive strength of concrete for different combinations

Type of superplasticizer	Dosage of superplasticizer (sp/c %)	Saturation dosage of sp (sp/c %)	Slump (mm)	Compressive strength		
				3 days N/mm^2	7 days N/mm^2	28 days N/mm^2
SNF-S1	0 (Reference)		0	39	45	56
	0.1	0.20	0	38	47	56
	0.2		25	39	49	58
	0.3		195	34	54	69
	0.4		bleeding	31	40	50
SNF-D2	0.1	0.23	10	47	57	62
	0.2		67	46	57	64
	0.25		100	40	55	63
	0.3		130	43	59	65
	0.4		165	37	56	67
SMF-S1	0.1	0.23	20	39	-	57
	0.2		32	45	55	69
	0.3		70	40	53	67
	0.5		158	41	52	73
	0.6		bleeding	40	52	60
	1		bleeding	45	-	53
PCE-D1	0.05	0.07	35	36	46	58
	0.1		120	42	47	54
	0.2		180	46	55	67
	0.3		bleeding	34	41	45

4.8 SUMMARY

An extensive study on paste, mortar and concrete aimed at establishing correlation between their behaviour has led to the following conclusions:

- The saturation dosages obtained for paste and mortars are comparable whereas a dosage slightly higher than the saturation dosage of paste was required for adequate workability in concrete due to the adsorption of some superplasticizer by the fines present in the coarse aggregate used here. The comparison of the cost of superplasticized concretes shows that a low-cost superplasticizer need not always result in cost-effective concrete, as the dosage of the superplasticizer for the optimum fluidity is also an important factor.

- The study of the flow behaviour of pastes at 60 minutes after mixing shows that loss of fluidity occurs for all the superplasticizers and dosages considered. If the fluidity of superplasticized paste at 60 minutes or at any other duration is more important than the immediate fluidity, the saturation dosage corresponding to that duration should, therefore be used in the mix design of concrete rather than arbitrarily overdosing the superplasticizer. In the case of mortar, the addition of sand results in higher loss of fluidity than in the paste, probably because of the absorption of superplasticizers by the fine aggregates. Generally, it was found that the SMF-S1 and PCE-D1 led to more slump loss than the SNF-S1 based concrete as observed in the case of corresponding paste. Also, as expected, the SNF with retarder was effective in limiting the slump loss of concrete.
- The Vicat penetration test results shows that the setting behaviour depends on the type of superplasticizer, and that the setting time is higher for the lignosulphonates and polycarboxylate than the sulphonated naphthalene-and melamine-based superplasticizers. A comparison of the penetration tests on paste and concrete indicates that the trend in the setting with different types of superplasticizers is almost same in both cases, and hence the test of paste can be used as a guideline in the selection for the superplasticizers for concrete in terms of setting time. Also, it is confirmed through the study that superplasticizers tend to retard the beginning of setting and do not necessarily prolong the setting process, i.e., the difference between the initial and final setting times are not affected.
- Electrical conductivity measurements on the superplasticized pastes have been used to characterize the setting behaviour, along with Vicat penetration measurements. It has been observed that the superplasticizer delays the initial

setting without prolonging the setting process, which is mainly manifested as an increase in the duration of the dormant stage.

- The study shows that the compressive strength can increase slightly due to the addition of superplasticizers, probably due to better compaction, especially at the saturation dosage of superplasticizer.

Generally, it can be concluded that the selection of the type and dosage of superplasticizer in concrete for high performance can be based on the test results from paste. This could lead to substantial savings in material and effort within the mix optimization process.

CHAPTER 5

EFFECT OF SUPERPLASTICIZER ON PROPERTIES OF HARDENED CEMENT PASTE

5.1 GENERAL

The study of the flow behaviour of superplasticized cements paste and its correlation with concrete shows that the fluidity and flow retention depend on the type and dosage of superplasticizers. The purpose of adding superplasticizers is to improve the fresh state properties of concrete without adversely affecting the hardened state properties. However, the literature shows that cement-superplasticizer incompatibility results in an adverse effect on the rate of hydration and hydrated products (Jolicoeur and Simard, 1998; Hanehara and Yamada, 2008; Agarwal et al., 2000; Prince et al., 2002; Nkinamubanzi and Aitcin, 2004; Bedard and Mailvaganam, 2005).

The objective of this chapter is to have an understanding on the influence of type of superplasticizers on the hydration behaviour and on the properties of hardened concrete. Indirect techniques like differential thermal analysis/ thermogravimetric/ differential thermogravimetric (DTA/TG/DTG) and X-ray diffraction study (XRD) give information about the average characteristics of the microstructure whereas direct methods like scanning electron microscopy (SEM) provide information about the way in which component phases are arranged in the microstructure (Scrivener, 1989; Ramachandran and Beaudoin, 2001).

The influence of superplasticizers on the hardened cement paste and more precisely, on the hydration processes and the microstructural development is explained in this Chapter. The cement paste phases are analyzed using XRD, micrographs, thermal analysis and nuclear magnetic resonance (Si NMR) for pure cement paste as well as for superplasticized pastes at saturation dosages. The complementary use of these approaches is intended to provide a complete picture of the hydration processes, with respect to the formation of new phases, the consumption of the anhydrous phases as well as the formation of C-S-H and C-H.

5.2 X-RAY DIFFRACTION (XRD) STUDY

5.2.1 Background

X-ray diffraction study helps to understand the influence of the incorporation of the superplasticizer on the hydration process of cement paste with respect to the consumption of crystalline anhydrous phases, as well as through the identification of crystalline products of hydration. The basic principle of XRD is that every crystalline substance gives a specific pattern; the same substance always gives the same pattern and in a mixture of substances each produces its pattern independently of others. When a beam of X-rays falls on a crystalline material, it is diffracted by the incidence angle given by Bragg's law:

$$2\, d \sin\theta = n\, \lambda \tag{5.1}$$

where d is the distance between the crystallographic planes, λ is the wavelength of the X-ray, n is an integer and θ is the diffraction angle.

XRD is used to identify the polycrystalline phases of hardened cement paste and superplasticized cement paste through the recognition of the X-ray patterns that are unique for each of the crystalline phases. So the technique allows the detection of ettringite (AF_t) and portlandite (C-H) along with the consumption of anhydrous phases of the cement (gypsum, C_3S, C_2S, C_3A, C_4AF, SiO_2 and $CaCO_3$).

Superplasticizers generally affect the hydration by the reduced formation of $Ca(OH)_2$ and ettringite in the initial ages of curing, which can be identified through XRD

(Singh et al., 1992; Mollah et al., 1995; Roncero, 2000; Prince et al., 2002; Roncero et al., 2002; Prince et al., 2003).

5.2.2 Materials Used and Sample Preparation

Cement C1 of 53 grade and 6 types of superplasticizers with properties as given in Section 3.2 along with a reference paste at several ages like half setting (corresponding to 20 mm Vicat penetration), 3, 7 and 28 days were tested. These ages are selected as reference ages so as to compare the effect of superplasticizers on the rate of hydration. The pastes were prepared with the saturation dosage of superplasticizers (determined from the Marsh cone test) and the mixing method adopted was the same as selected from Section 3.4. The samples were cured under water and the cement paste samples of 50mm×50mm×10mm were cut and kept in acetone to prevent the hydration after the required age. Just before each test, the samples were dried in an oven at 60°C and the surface was polished to remove undulations. To account for the variations in the preparation of sample and the instrument intensity, a standard sample of aluminium foil was placed over the specimen and the normalized intensity was used for comparison purposes.

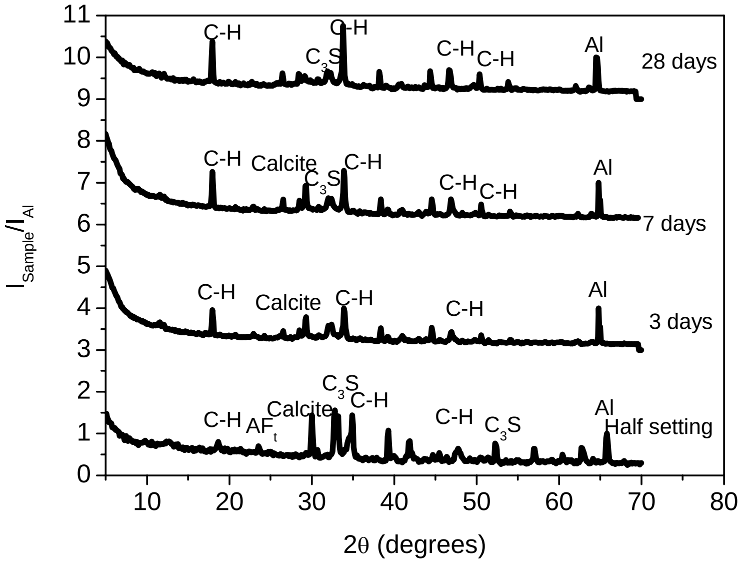
5.2.3 Experimental Procedure

The XRD analysis was performed with a Bruker D8 Discover powder diffractometer. In this apparatus, the Cu K_α (λ = 1.5418Å) radiation is generated in a Cu tube at 35kV, 25 mA. The tests were performed over a Bragg angle (2θ) range of 5-70° with a scan speed of 1 sec per step on the samples. The ratio of the intensity of sample to the intensity of aluminium at a particular Bragg angle is taken for the comparison of crystalline phases of superplasticized pastes.

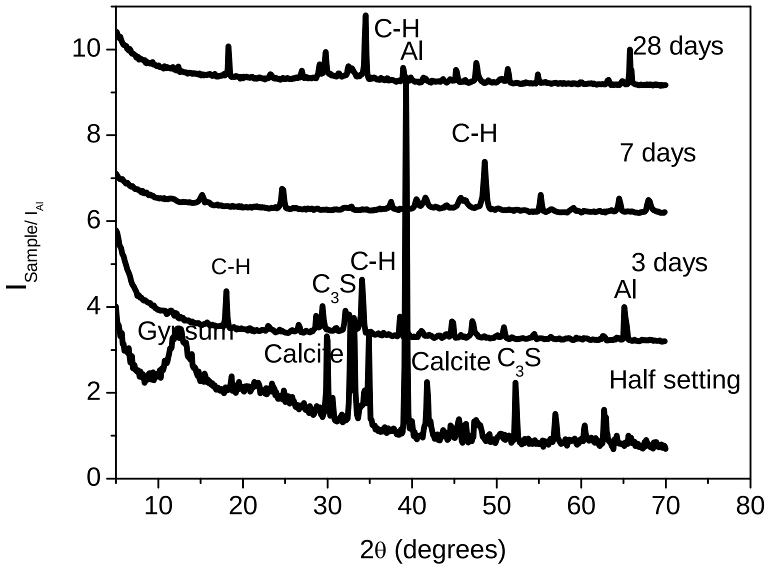
5.2.4 Results and discussions

The XRD pattern of cement paste and superplasticized pastes for half setting, 3, 7 and 28 days are shown in Figure 5.1 (a-g). The relative evolution with age of the identified crystalline phases like C_3S, gypsum, ettringite and portlandite can be compared with the intensity. In the case of pure cement paste, amount of unhydrated phases decrease with an increase in the age of curing and C-H increases with the age of curing, as shown in the X-ray diffractograms. Ettringite is present at half setting and disappears after 3 days as expected. The peak of calcite ($CaCO_3$) indicates the occurrence of carbonation in all the samples.

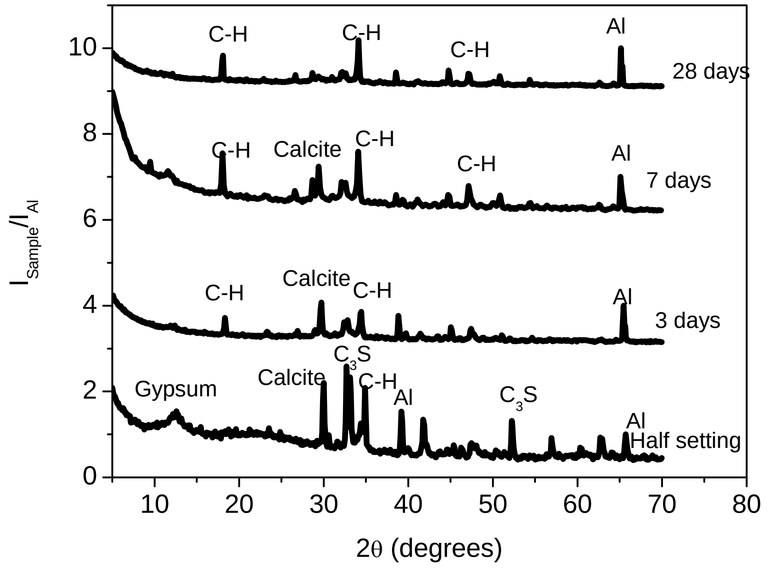
The XRD pattern of superplasticized paste shows some qualitative differences in the hydration rate due to the incorporation of superplasticizers which is supported by the reported results (Mollah et al., 1995, Roncero, 2000; Prince et al., 2003). This qualitative difference varies with different superplasticizers. The delay of C_3A hydration in the presence of superplasticizers is obvious through the absence of ettringite at half setting in the XRD pattern of superplasticized pastes. It affects the setting and hardening due to the formation of electrical double layer along with "the diffuse ion swarm" of superplasticizers on Ca^{2+} ions preventing the hydration (Mollah et al., 1995).



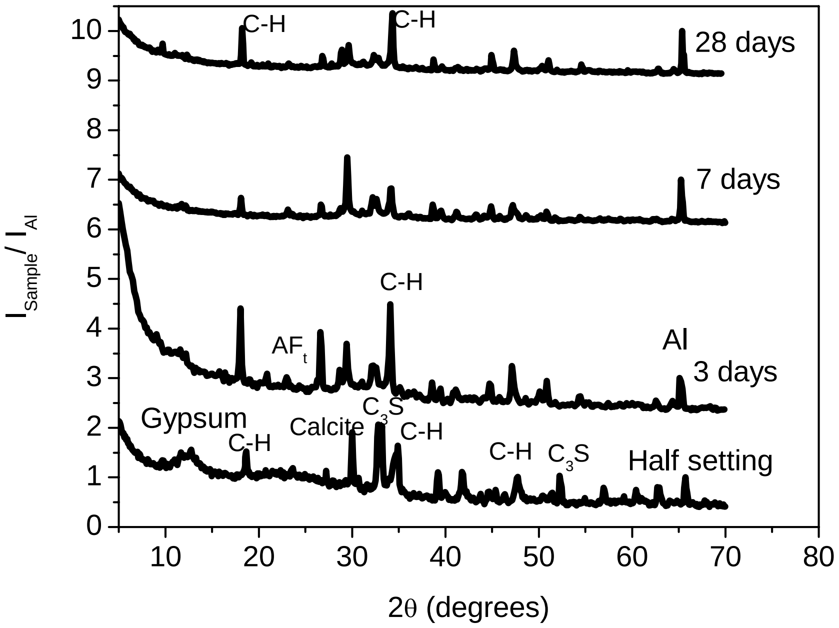
(a) Cement paste with w/c 0.35



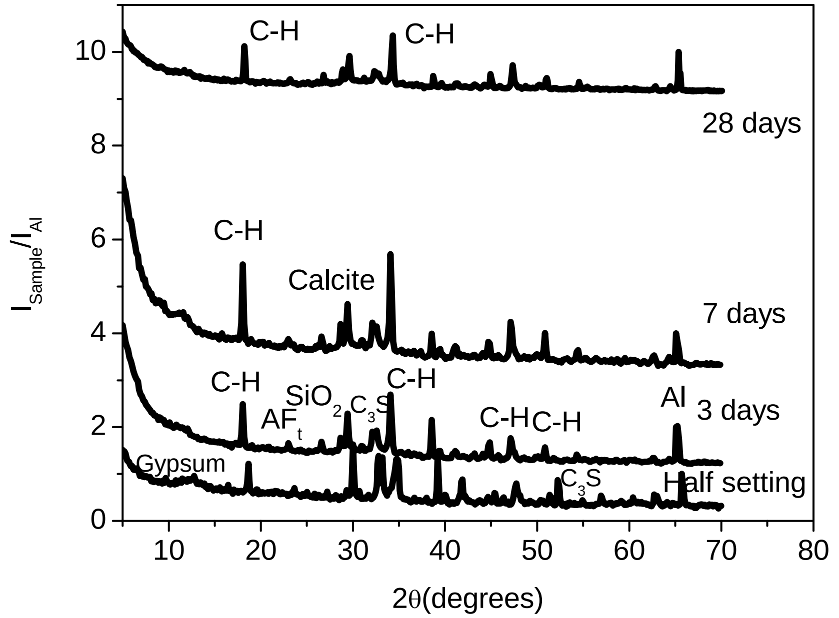
(b) LS-C1 based paste



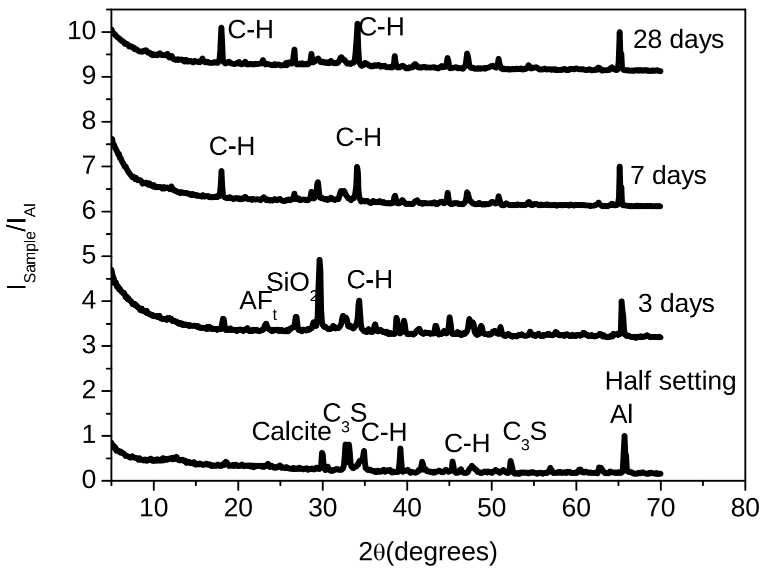
(c) SNF-S1 based paste



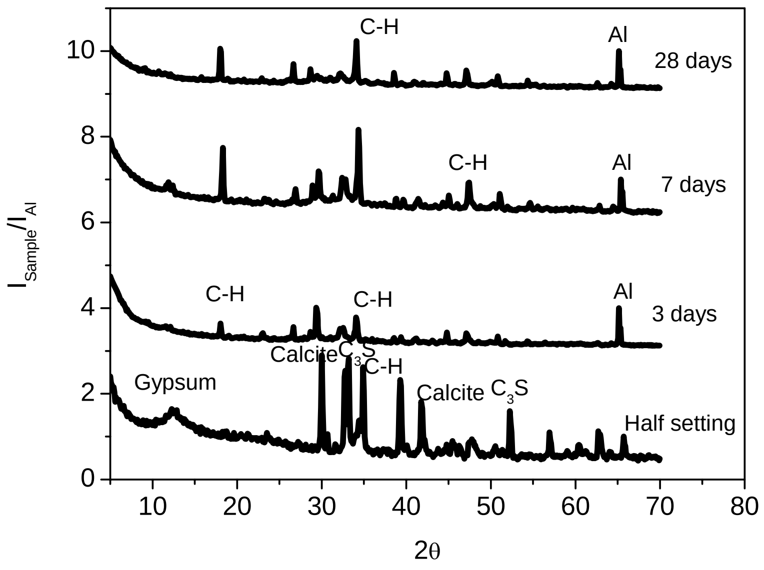
(d) SNF-D2 based paste



(e) SNF-C2 based paste



(f) SMF-S1 based paste



(g) PCE-D1 based paste

Fig. 5.1 (a-g) X-ray diffractogram of cement paste and superplasticized cement paste

The trends of the evolution of the crystalline phases of pure cement paste and superplasticized cement paste at different ages are summarized in Table 5.1. The arrows indicate the relative change in the amount of the crystalline phases observed. The amount of unhydrated compounds like C_3S/C_2S decreases with an increase in the age of curing. Even though the time of half setting is different for the studied pastes, major qualitative difference could not be observed between the superplasticized pastes. The presence of portlandite in the superplasticized cement pastes at half setting indicates that the formation of portlandite is not affected by the superplasticizers. Generally, the amount of portlandite increases with age of curing, as expected. However, anomaly is observed with some types of superplasticizers.

Table 5.1 Relative evolution of the crystalline phases with age

Type of paste	Age	C_3S, C_2S	SiO_2	Gypsum	Ettringite	Portlandite
Reference	Half setting	P	P	A	P	P
	3 days	P↓	P	A	A	P
	7 days	P↓	P	A	A	P ↑
	28 days	P ↓	P↓	A	A	P ↑
LS-C1	Half setting	P	P	P	A	P
	3 days	P	P	A	P	P
	7 days	P	P	P	A	P ↑
	28 days	P	P	A	A	P ↑
SNF-S1	Half setting	P	P	P	A	P
	3 days	P	P	A	P	P
	7 days	P	P	A	P	P
	28 days	P	P	A	P	P
SNF-D2	Half setting	P	A	P	A	P
	3 days	P	P	A	P	P
	7 days	P	P	A	P	P
	28 days	P	P	A	P	P ↑
SMF-S1	Half setting	P	P	P	A	P
	3 days	P	P	A	P	P
	7 days	P↓	P	A	P	P ↑
	28 days	P	P	A	P	P ↑
SNF-C2	Half setting	P	A	P	A	P
	3 days	P	A	A	P	P
	7 days	P	A	A	A	P
	28 days	P	P	A	P	P
PCE-D1	Half setting	P	A	P	A	P
	3 days	P	P	A	P	P
	7 days	P	P	P	P	P ↑
	28 days	P	P	A	P	P

P - present; A – absent

↑ ↓Increase or decrease of the phase, respectively, with reference to the previous age

The comparison of the diffractograms of pure cement paste with superplasticized pastes at half setting indicates that superplasticizer mainly affects the hydration of C_3A and consequently the formation of ettringite; it can be observed that no gypsum is present in the pure cement paste at half setting due to its conversion to ettringite by reacting with C_3A. However, in the superplasticized pastes, no traces of ettringite were observed at half setting; instead, gypsum is present. This clearly shows that the setting is retarded due to the addition of superplasticizers because it inhibits the hydration reaction. The possible reasons for set retardation have been already explained in Chapter 2. The results also support the data from the setting time tests reported in Chapter 4.

Also, traces of ettringite are present upto 28 days in all the superplasticized pastes except for the paste with LS-C1, in which it is present upto 3 days only. However, the peak intensity of ettringite decreases between 3 days and 7 days and again increases after 7 days in the case of SMF-S1 and PCE-D1. This is in accordance with the reported results (Prince et al., 2003) that the addition of superplasticizer affects the crystallization of primary ettringite and when no more superplasticizer is available to block the natural growth of ettringite, it reappears after 28 days. The diffraction pattern does not show any traces of AF_m or secondary gypsum phases which indicate that phase reversal (see Chapter 2) has not occurred. In short, from the diffractograms observed in the particular cementitious system under study, it is seen that there is very strong interaction between the superplasticizer and ettringite at early ages.

5.3 SCANNING ELECTRON MICROSCOPY (SEM)

5.3.1 Background

Backscattering electron (BSE) imaging is generally used to identify the different phases of hardened cement paste and to understand the development of the microstructure of cement paste. Scrivener (1989) has used the technique to distinguish between the dense and porous phases in the microstructure of same paste. The basic principle is that the electrons of the incident beam, rebound from the surface of the specimen depending on the composition of the phases. The intensity of the BSE signal is a function of the average atomic number of the sample and the contrast observed is based on the atomic number of phases (Famy et al., 2002).

The unhydrated particles have higher molecular weight with higher back scattering intensity than hydrated particles (Zhao and Darwin, 1992; Puertas et al., 2005). In such studies it has been shown that C_4AF has the highest intensity, C-H is brighter than C-S-H and that the pores appear black.

A comparative study of the microstructure of different superplasticized cement pastes and reference pastes is conducted here to understand the influence of different types of superplasticizers on the hydration process and consequently on the development of microstructure.

5.3.2 Sample Preparation

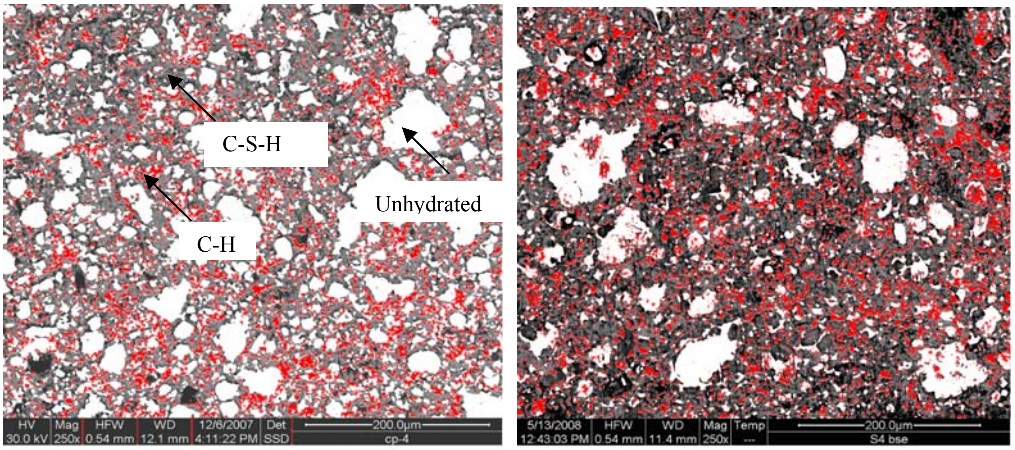
The quality of the BSE image depends on the sample surface. A highly polished surface is required for BSE microscopy (Scrivener, 1989). The sample preparation included the preparation of cement paste samples, curing for the prescribed ages, cutting, grinding and polishing. The superplasticized cement paste cubes with four families of superplasticizers along with the reference paste cubes were prepared as in the case of the XRD study. The cubes were cured under water for 3, 7 and 28 days. After the period of curing, the samples were put in acetone to remove the pore water by the solvent replacement method to prevent further hydration as in Roncero (2000). Samples of 10mm×10mm×10mm were cut and carefully ground by hand at moderate pressure on a middle-speed lap wheel with p800, p1000, p1200, p1600 and p2000 sand papers. Afterwards, lap wheel with 6-12, 3-6 and ½ -1 μm diamond paste was used to get a fine polished surface.

5.3.3 Comparison of the Microstructure of Superplasticized Paste and Reference Paste

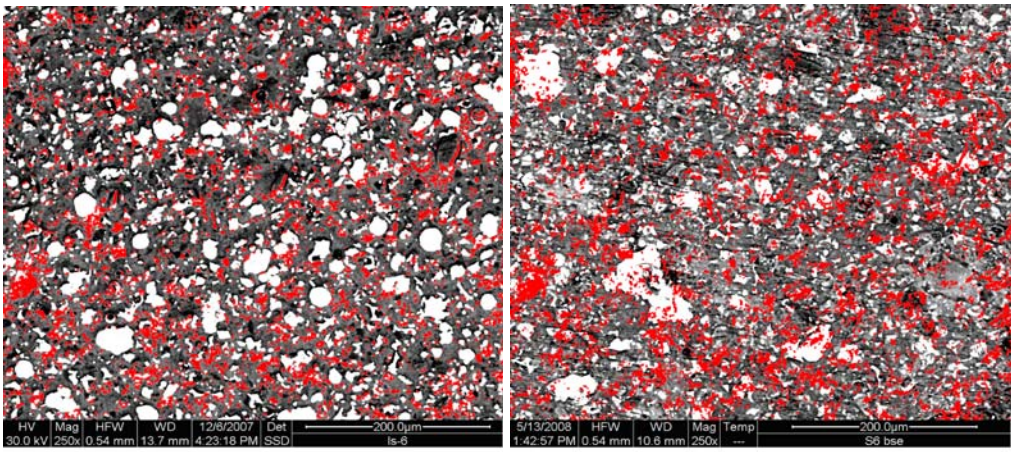
The microstructural study was performed on pastes with no admixture (i.e., reference paste) and those containing saturation dosages of superplasticizers. The BSE micrographs of reference paste and paste with LS-C1, SMF-S1, PCE-D1 and SNF-S1 based superplasticizer are shown in Figure 5.2 (a-i). The microstructure of cement paste shows the bright grains of unhydrated cement, the intermediate gray of C-S-H and slightly brighter gray (shown as red for easy identification) of calcium hydroxide, along with dark pores. As the age of curing increases up to 28 days (see Figure 5.2 a and b), the amount of unhydrated particles decreases and a uniform distribution of hydrated particles is identified in the picture.

The BSE morphological analysis of superplasticized pastes showed no substantial difference in either the form or the texture of the different hydration products in pastes with and without admixtures. However, superplasticized pastes show more amount of unhydrated particles at 3 days than reference paste confirming the retardation of hydration in early ages due to the incorporation of superplasticizers as already discussed in Chapters 2 and 3. Even though, the micrographs are obtained at the saturation dosage of superplasticizers, the amount of unhydrated particles is different for different pastes. In the case of LS based superplasticizer, more amount of C-S-H can be observed. The amount of unhydrated products is more for the paste with the SMF at 3 days compared to that with the PCE. More unhydrated particles than in the pastes with SMF and PCE can be observed in the paste with SNF at 28 days. Also, the pastes with the SMF micrograph shows more C-H at 28 days, compared to those of the other superplasticizers.

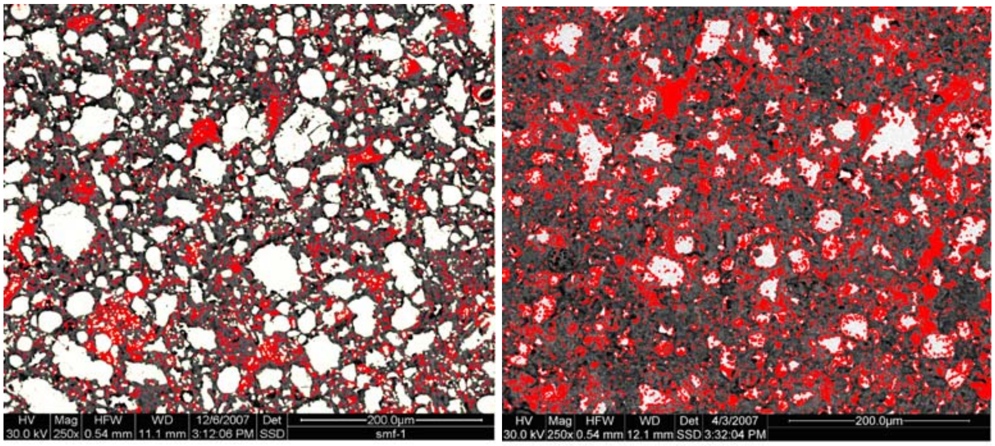
A comparison of the microstructure of the pastes with SMF and PCE shows that a more uniform microstructure is produced in the latter case. The number of pores in the superplasticized paste is more than in the reference paste and it is higher in the paste with PCE. The pores are smaller when PCE is added as reported by Sakai et al. (2006). Generally, the increase in strength due to the addition of superplasticizer can be attributed to making the microstructure more dense, uniform and compact (Uchikawa, et al., 1995). The micrographs shown in Fig. 5.2 also support the modification of the microstructure with uniform distribution of C-S-H and C-H



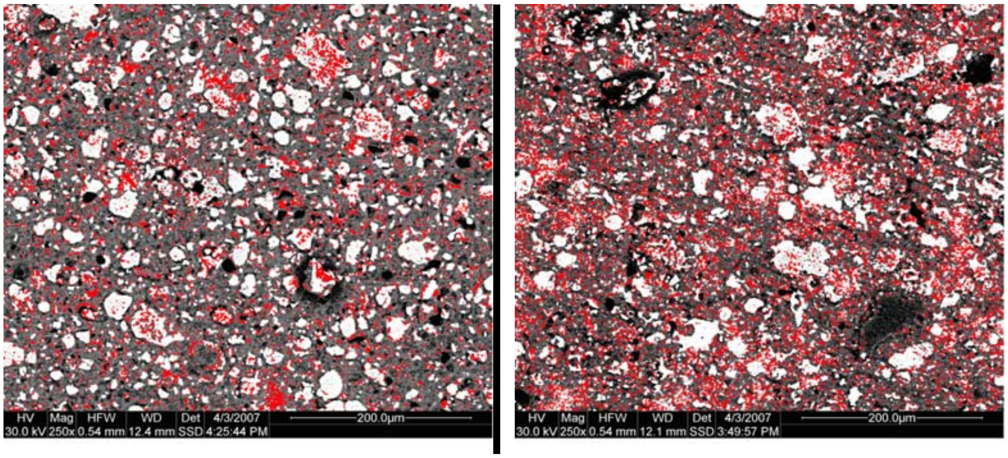
(a) Reference paste, 3 days (b) Reference paste, 28 days



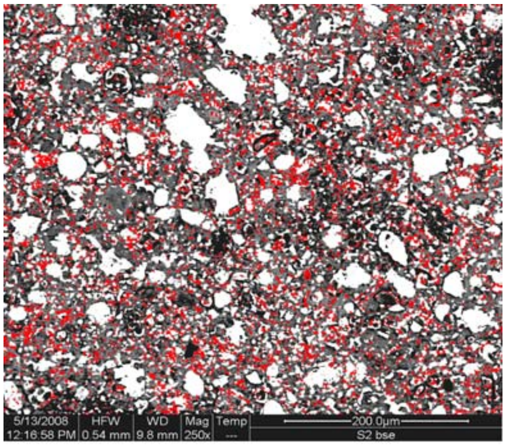
(c) LS-C1 based paste, 3 days (d) LS-C1 based paste, 28 days



(e) SMF-S1 based paste, 3 days (f) SMF-S1 based paste, 28 days



(g) PCE-D1 based paste, 3 days (h) PCE-D1 based paste, 28 days

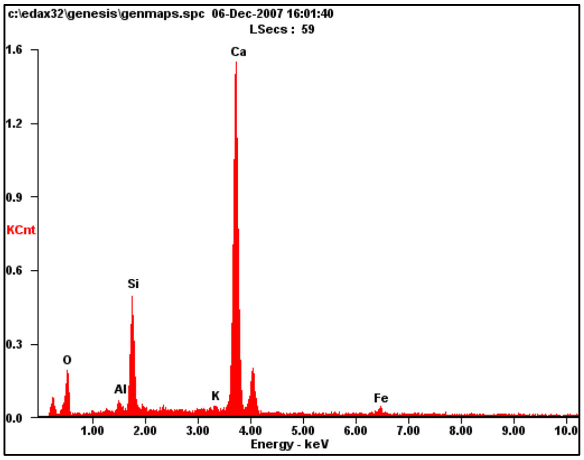


(i) SNF-S1 based paste, 28 days

Fig. 5.2 (a-i) BSE (250X) micrograph of pure cement paste and superplasticized cement paste

Energy dispersive X-ray analysis (EDAX) was also done for the selected samples to find out the elemental composition of different phases. It is a technique used for identifying the elemental composition of the specimen, or an area of interest thereof. Each of the peaks in an EDAX spectrum is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. An EDAX spectrum not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as K-alpha peak or K-beta peak.

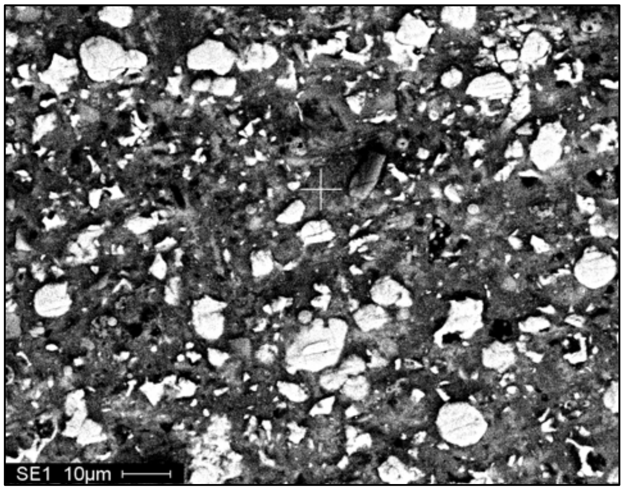
Figure 5.3 (a-c) shows an example of the BSEM micrograph along with the EDAX spectrum of a C-S-H particle for the paste with the lignosulphonate. The elemental composition of Ca and Si in the EDAX confirms the presence of C-S-H in the micrograph. The Ca/Si ratio can also be determined for validating the identified phases through the microstructure. A higher value of Ca/Si ratio for C-S-H in some cases of superplasticized pastes shows that it is more amorphous than the pure cement paste (Taylor, 1997). However, the summary of the results is not reported in this study as the numbers of studied samples are limited.



Element	***Wt%***	***At%***
OK	40.83	61.13
AlK	01.76	01.56
SiK	12.88	10.99
KK	00.84	00.51
CaK	41.86	25.02
FeK	01.83	00.78

(a) EDAX spectrum of different elements in the selected spot

(b) Elemental composition corresponding to (K_α) radiation



(c) Micrograph of C-S-H particle

Fig. 5.3 (a-c) BSE micrograph along with EDAX for a dark grey (C-S-H) particle in the LS based paste

5.4 THERMAL (DTA/TG/ DTG) ANALYSIS

5.4.1 Background

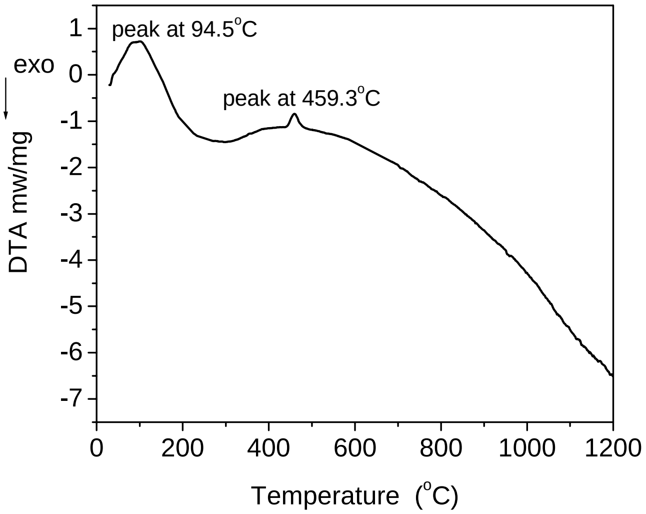
Differential thermal analysis (DTA) along with thermogravimetric (TG) and differential thermogravimetric analysis (DTG) can be used to understand the hydration reactions of superplasticized cement paste (Prince et al., 2002). The basic principle is that the material is subjected to continuous heating at a uniform rate and the loss in mass is studied. In DTA, the difference in temperature (ΔT) between the sample and reference material such as α-Al_2O_3 is recorded while both are subjected to the same heating program (Ramachandran and Beaudoin, 2001).

TGA measures the loss in weight as the temperature of the substance is raised at a uniform rate. The reactions occurring at the heating process are responsible for the changes in weight. Knowing that certain reactions occur at specific temperatures enables the identification of the constituents of the sample. TGA curves are usually used to measure the weight loss corresponding to thermal decomposition whereas DTG analysis helps locate the temperature peak due to the decomposition of different phases in cement pastes.

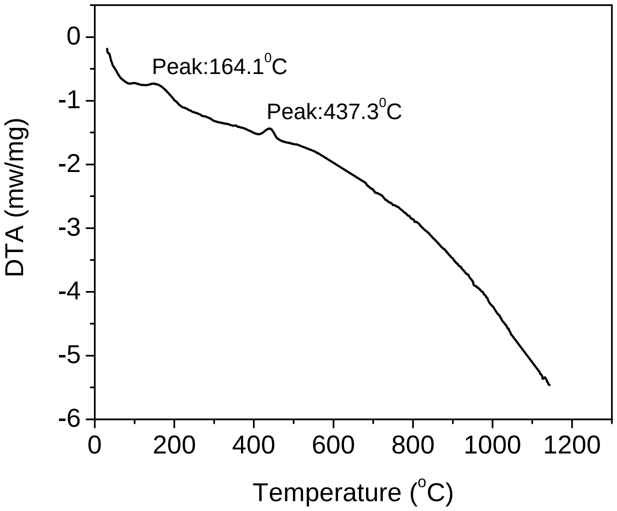
5.4.2 Result and Discussions

The analyses were conducted with a NETZSCH STA 409 C/CD, in nitrogen atmosphere, within a temperature range of 20-1400 ºC, at a uniform rate of 10 K/min. The samples were obtained by powdering the prepared paste fragments and sieving through 70 μm sieves.

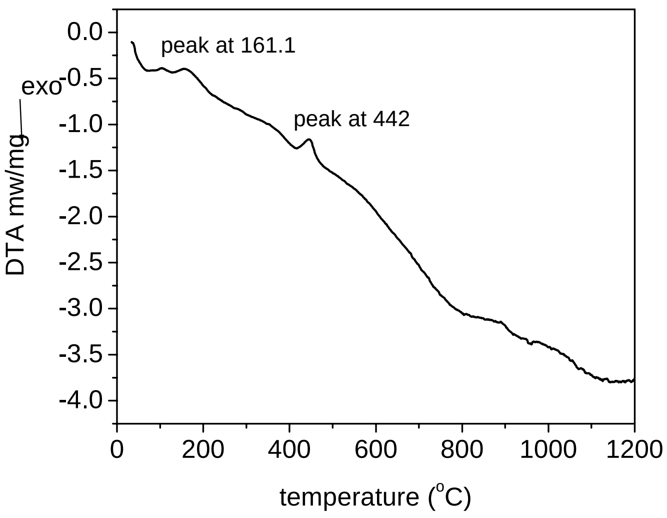
Figure 5.4 (a-c) shows the DTA analysis of superplasticized paste and reference paste after 3 days of curing. The small endothermic peak at 94.5ºC for pure cement paste corresponds to dehydration of the non-evaporable water from the C-S-H gel (Prince et al., 2002, 2003). In the case of pastes with SMF and PCE, an endothermic peak at about 160ºC shows the decomposition of ettringite, gypsum and C-S-H gel (Prince et al., 2003). The increase in the intensity of this effect with time is indicative of increased formation of C-S-H with time. The endothermic peak in the range of 425-550ºC shows the decomposition of C-H, in all the three cases (Tzouvalas et al., 2005; Zhang, 2007).



(a) Reference paste, 3 days



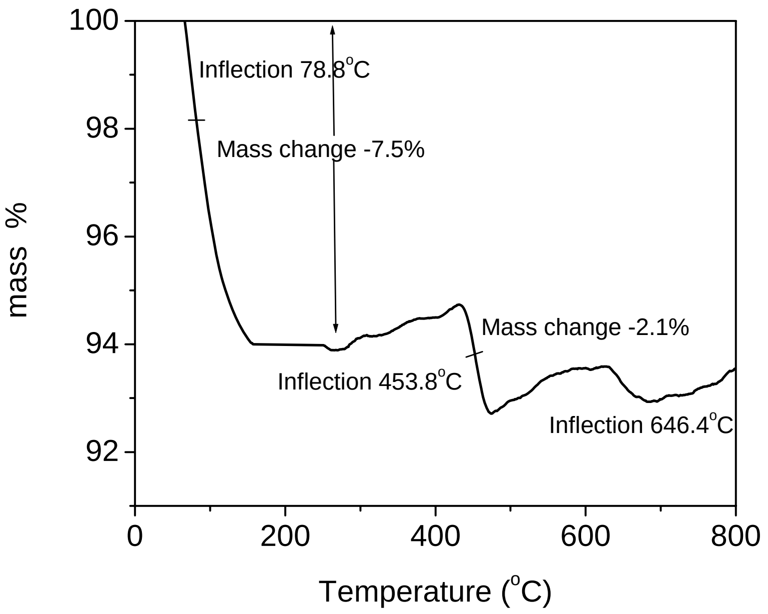
(b) Paste with SMF-S1, 3 days



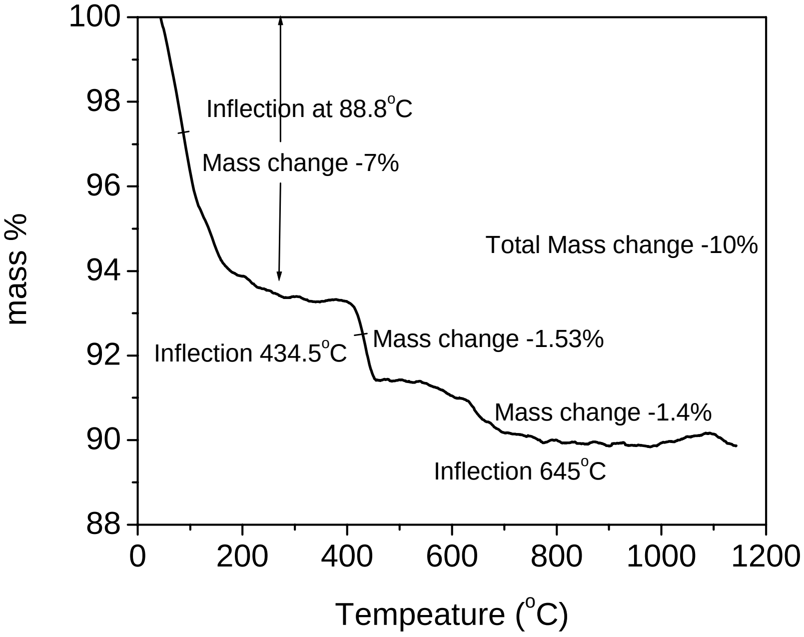
(c) Paste with PCE-D1, 3 days

Fig.5.4 DTA analysis of cement paste and superplasticized paste at 3 days

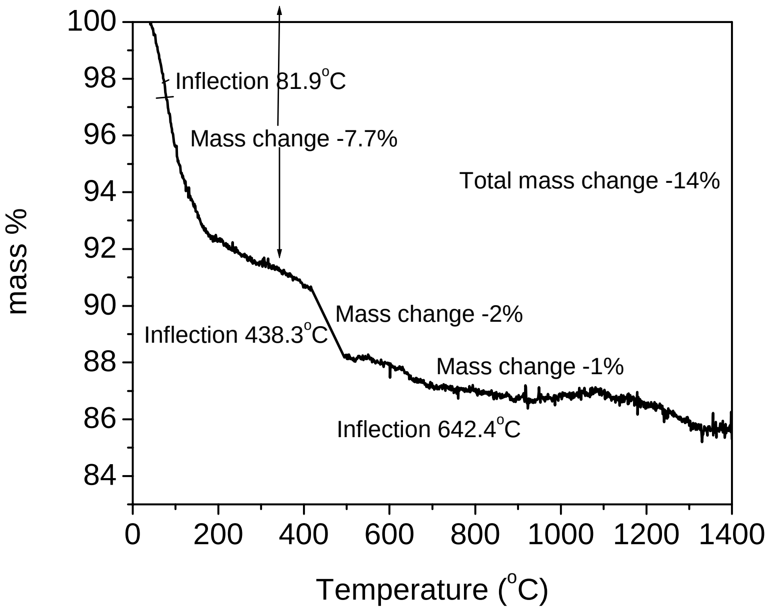
Figure 5.5 (a-d) shows the TG curves of the different pastes at 3 days. The total loss in mass represents the degree of hydration of the pastes. The quantity of calcium hydroxide is calculated from the weight loss at the temperature around 450-550ºC. The loss in mass for superplasticized paste is less than that of pure cement paste at 3 days showing that the formation of C-H is slightly retarded at early ages due to the presence of superplasticizers. This is in accordance with the reported results of Ramachandran et al. (1995) and Puertas et al. (2005). The mass loss is small and within the ranges of the reported results (Prince et al., 2002; Prince et al., 2003; Puertas et al., 2005).



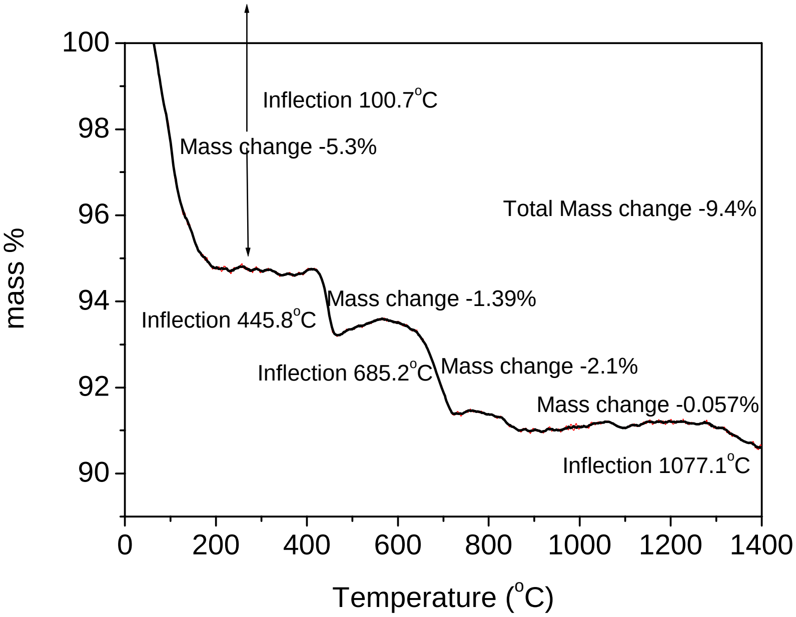
(a) Reference paste, 3 days



(b) Paste with SMF-S1, 3 days



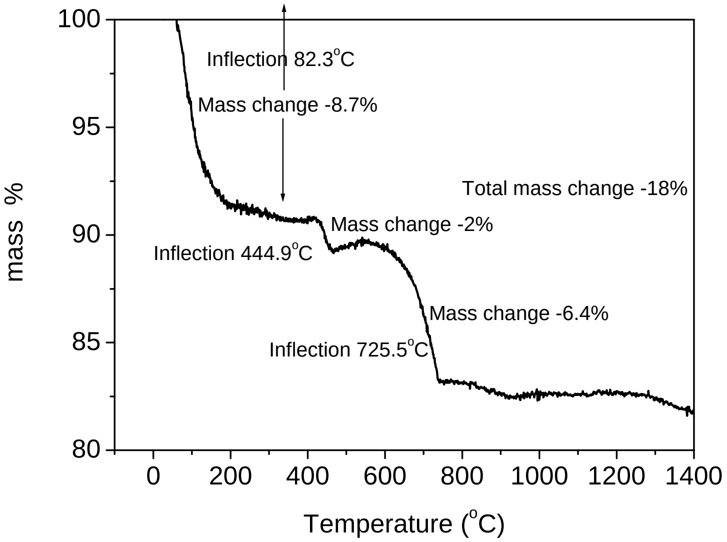
(c) Paste with PCE-D1, 3 days



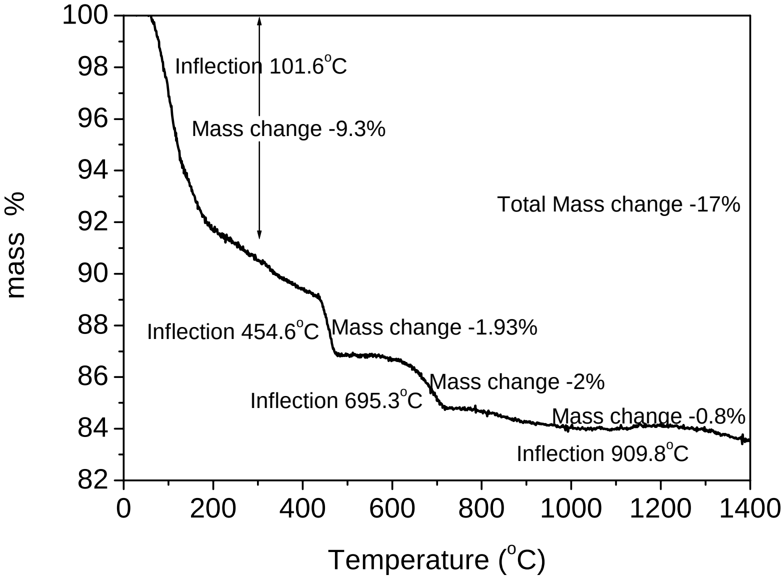
(d) Paste with SNF-C2, 3 days

Fig. 5.5 (a-d) TG and DTG analysis of pastes at 3 days

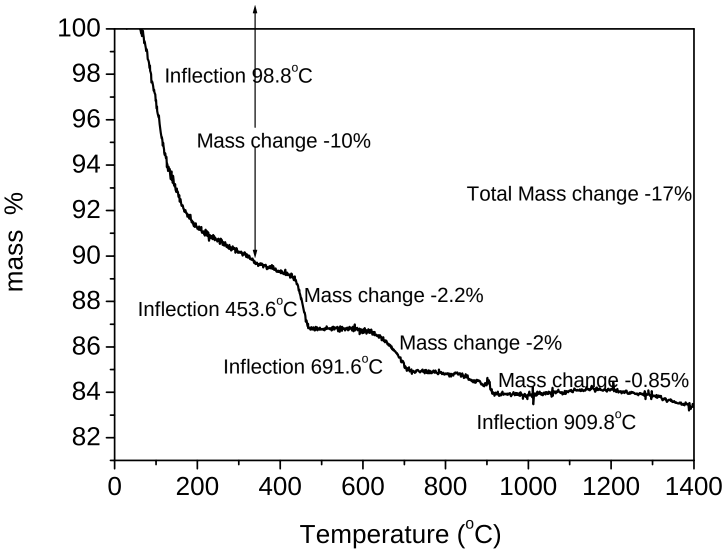
The results of the TG/DTG analysis for different pastes at 28 days are shown in Figure 5.6 (a-d). The total mass loss increases in all cases with age of curing. The mass loss corresponding to 600-800 ºC for the pastes at 3 and 28 days, is generally interpreted as partly due to carbonation and partly to the final stages of dehydration of C-S-H and the hydrated aluminate phases (Taylor, 1997). However, the XRD results confirmed the presence of calcite; hence, this loss is mainly due to the dehydration of C-S-H, hydrated aluminate phases and calcites.



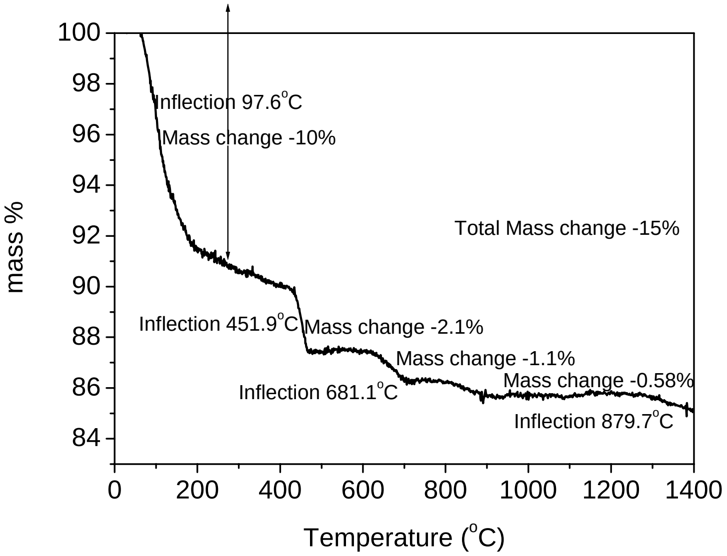
(a) Reference paste, 28 days



(b) Paste with SMF-S1, 28 days



(c) Paste with PCE-D1, 28 days



(d) Paste with SNF-C2, 28 days

Fig. 5.6 TG and DTG analysis of pastes at 28 days

Table 5.3 gives the summary of total mass loss, as well as the mass loss corresponding to the decomposition of C-H at the temperature of around 450-550 ºC. It is observed that the total mass loss increases with the age in all the cases whereas the mass loss corresponding to C-H decomposition is comparable at 3 days and 28 days. This shows that the superplasticizers retards the hydration mainly in the initial stage. However, the percentage mass loss corresponding to the decomposition of C-H at 3 days and 28 days for different combinations seems to be too small for a detailed interpretation.

Table 5.2 Summary of mass loss in different pastes

Type of mix	Mass loss corresponding to the decomposition of C-H (%)		Total mass loss (%)	
	3 days	28 days	3 days	28 days
Pure Cement paste	2.1	2	*	18
Paste with SMF-S1	1.5	1.9	10	17
Paste with PCE-D1	2.0	2.2	14	17
Paste with SNF-C2	1.4	2.1	9.4	15

*Could not be determined

5.5 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (Si NMR)

5.5.1 Background

Nuclear magnetic resonance spectroscopy is a technique used to characterize the state of polymerization of silicates in the cement paste. NMR determines the energy (resonance absorption) needed to invert the nuclear spin in Si atoms due to a powerful alternating magnetic field. Magic angle spinning (MAS) NMR is a technique used on solid phases, which consists of spinning the sample at high frequencies at the magic angle of 54°44’ to the magnetic field (Roncero, 2000; Roncero et al., 2002; Puertas et al., 2005).

The MAS NMR of siliceous materials provides useful information about the state of the SiO_4^{4-} tetrahedrons. The Si MAS NMR spectra exhibit peaks at 5 different chemical shifts that correspond to the different electronic environments of the Si atom, which are affected by the length of the Si-O bond, the Si-O-Si angle and the nature of neighbouring atoms. The chemical shifts depend on the number of oxygen atoms shared by the tetrahedral, known as the degree of condensation of the tetrahedra. Each type of tetrahedron connectivity is denoted as Q^n, where n denotes the number of shared oxygen atoms. Thus, the five chemical shifts are Q^0, Q^1, Q^2, Q^3, Q^4 in which the Si tetrahedra share 0, 1, 2, 3 and 4 oxygen atoms, respectively, with other Si atoms.

Table 5.4 shows the chemical shifts corresponding to the five electron environments described above. The anhydrous silicate phases of the cement (C_3S, C_2S) correspond to the monomer state (Q^0), which undergoes polymerization as the hydration proceeds. The hydrated cement pastes manifest the presence of Q^1 and Q^2 tetrahedrons. The Q^1 and Q^2 peaks correspond to the formation of the C-S-H gel, the structure of which is formed mainly by 3n-1 long chains of tetrahedrons.

Table 5.3 Ranges of ^{29}Si chemical shifts of the Q^n tetrahedrons

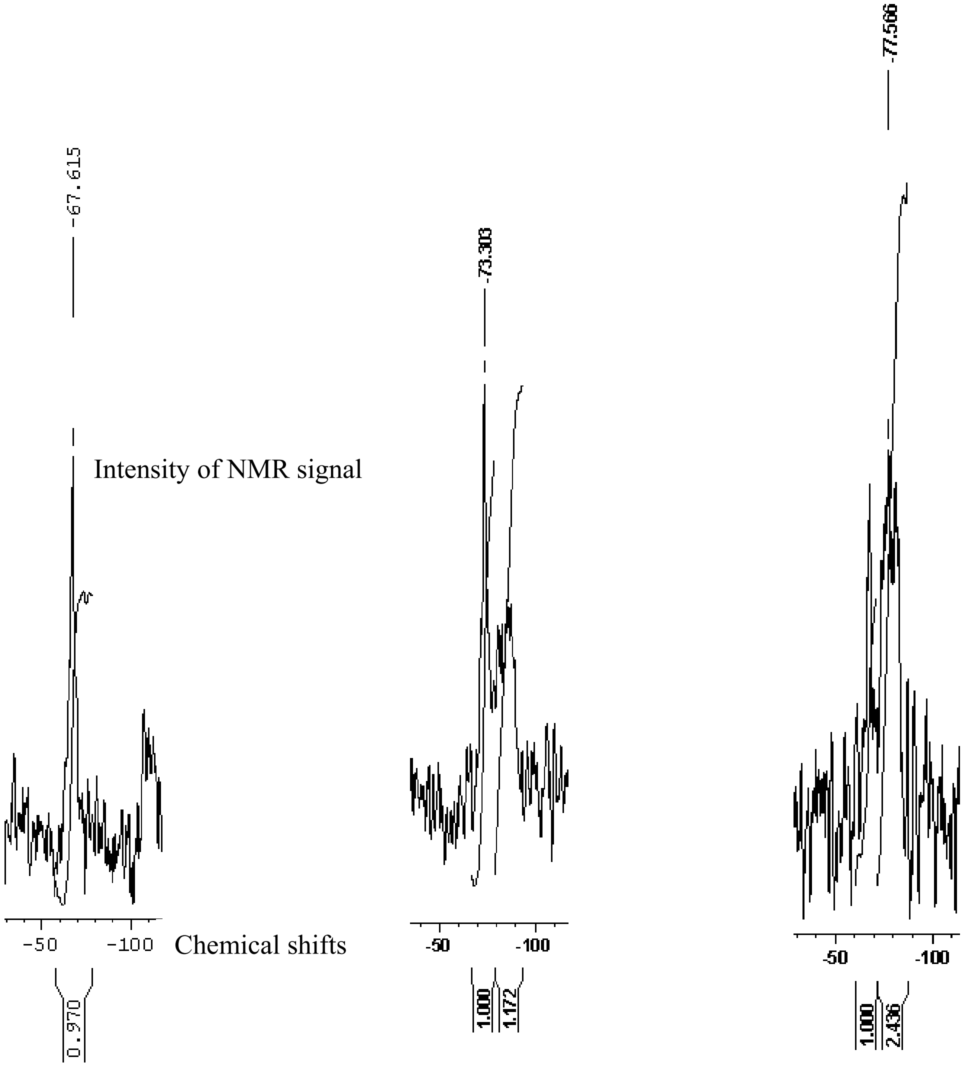
Ranges of chemical shifts (ppm)				
Q^0	Q^1	Q^2	Q^3	Q^4
-66 to -74	-75 to -82	-85 to -89	-95 to -100	-103 to -115

5.5.2 Sample Preparation

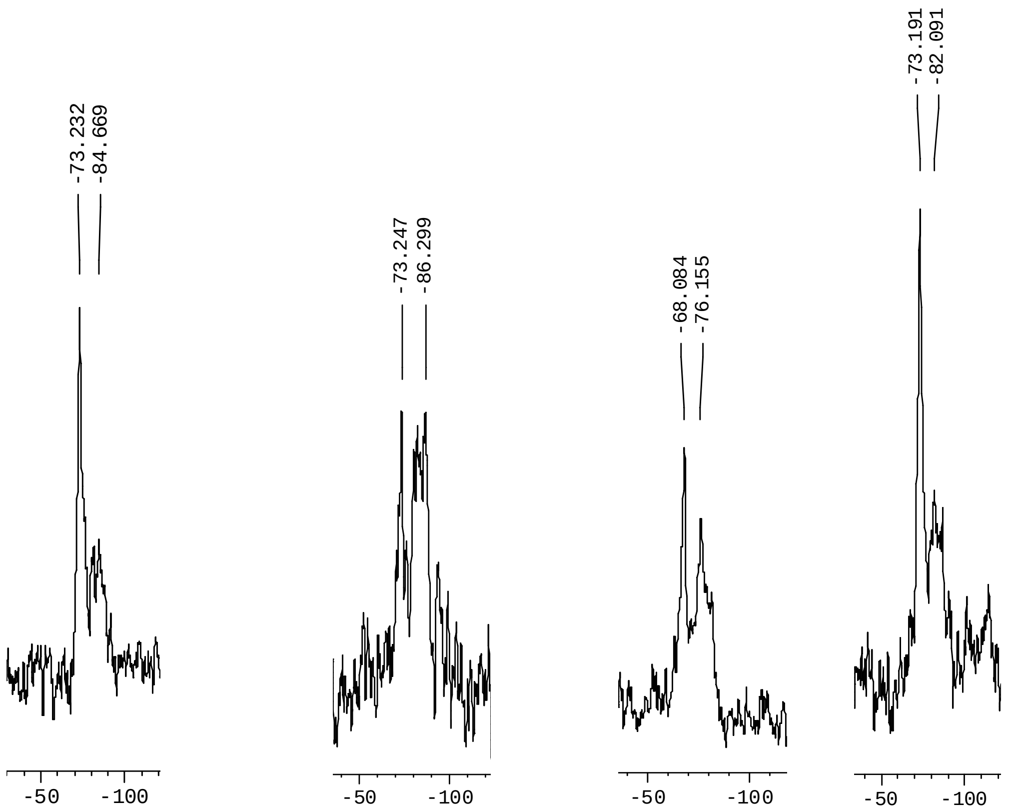
The preparation of the sample was the same as that in the case of the DTA/TG analysis. Tests were conducted on selected pastes at half setting, 3 days and 28 days. The powdered sample was kept in air tight containers till the date of testing.

5.5.3 Results and Discussions

A Bruker BZH 300 solid state high resolution spectrometer was used for the ^{29}Si NMR of the pastes. Tetramethylsilane (TMS) was used as the reference material, and the chemical shifts were determined with reference to that of the TMS. The details of the Si NMR spectrum of reference paste, along with superplasticized pastes are given in Figure 5.7 (a-g). The chemical shifts are represented along the horizontal axis and the magnitude or intensity of the NMR resonance signal is displayed along the vertical axis of the spectrum and it is proportional to the molar concentration of the sample. It is observed that at half-setting, the peak corresponding to Q^0 is identified in all the pastes showing the anhydrous silicate phases of the cement (C_3S, C_2S) corresponding to the monomer state. Two peaks corresponding to Q^0 and Q^1 can be identified in the studied pastes for 3 days and 28 days. The peaks shows that the amount of dimer gradually increases with a reduction in monomeric silicates for 3 to 28 days. Q^2 units were detected in the case of paste with SMF at 28 days compared to the paste with PCE. This indicates that the retardation in hydration due to SMF is less than that with PCE.



(a) Cement paste, half setting (b) Cement paste, 3 days (c) Cement paste, 28 days



(d) and (e) SMF based paste, 3 and 28days (f) and (g) PCE based paste, 3 and 28days

Fig. 5.7 Details of Si NMR spectrum of different pastes for different ages

The relative concentration of the Q^n units can be determined by the integration of their corresponding curves. Since the Q^0 and Q^1 peaks in the NMR spectra overlap, the areas corresponding to the Q^0 and Q^1 peaks, denoted as A_0 and A_1, respectively, are obtained for each spectrum as in Figure 5.8.

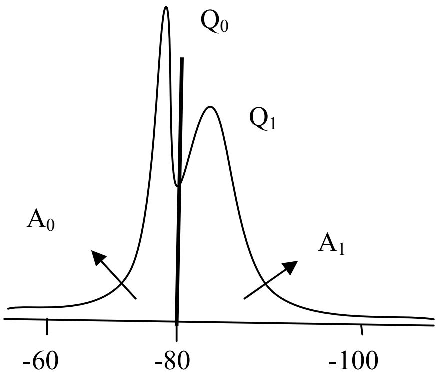


Fig. 5.8 Determination of area of peaks of the Si NMR spectrum

The relative area of the Q^1 peak (A_1/A_0) ratios for each paste is shown in Figure 5.9. It can be observed that the superplasticizer has a significant effect on the polymerization of the silicates during the hydration process. Its incorporation leads to the formation of a lower amount of dimers at 3 days as well as at 28 days, reflected by the lower relative areas of Q^1 peak in all the superplasticized pastes compared to reference paste.

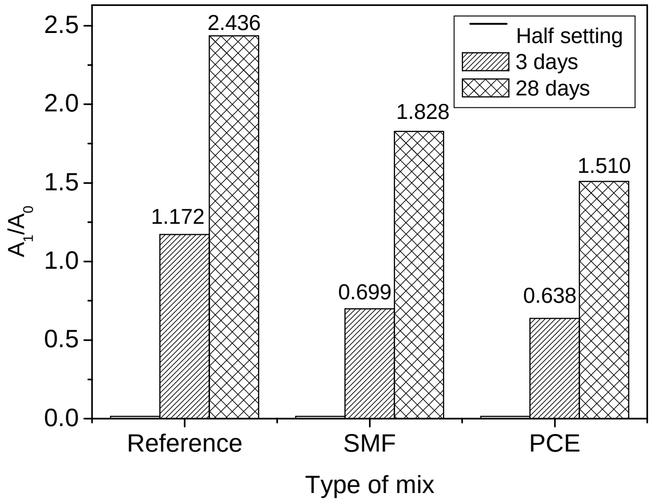


Fig. 5.9 Comparison of area of the Q^1 peak (A_1) with reference to the area of the Q^0 peak (A_0) at different ages

It is observed that the silicate polymerization is more in the paste with SMF than in the paste with PCE i.e., (A_1/A_0) is more for SMF). The results obtained from setting tests also supports this result as the setting time for the paste with PCE was more than that for the paste with SMF. Further to this, the change in the relative area of peaks indicates a change in the C-S-H morphology in the presence of superplasticizers.

5.6 SUMMARY

A multiple technique based approach, instead of a single test method, is used for studying the effect of the superplasticizer type on the hydration and the microstructural development for a better understanding of the influence of the incorporation of superplasticizers on the hardened properties. The comparison of X-ray diffractograms of the reference paste and superplasticized paste shows that the superplasticizers mainly influence the hydration of aluminates and consequently the formation of ettringite rather than the formation of portlandites. However, the quantitative analysis based on the thermal techniques shows that the amount of C-H formed for superplasticized pastes is less than that of reference paste at 3 days

Also, the retardation in hydration in the presence of superplasticizers can be observed through the BSE images, in which the amount of unhydrated particles in the superplasticized paste is more than that in the reference paste. Also, a lower polymerization of the silicates has been observed through the NMR study, in the presence of the superplasticizer, which is reflected by lower proportion of dimers at the age of 3 and 28 days. In addition, the silicate polymerization is also affected by the type of superplasticizer; the paste with PCE has a lower amount of dimers compared to the paste with the SMF. This has been observed in setting tests in which PCE retarded the setting more than the SMF.

Even though the polymerization of C-S-H is lower in the superplasticized pastes, a slight increase in compressive strength due the incorporation of superplasticizer was observed (see Section 4.7); it appears that the mechanical behaviour is dependent more on the dense and uniform microstructure developed in the superplasticized pastes. Hence, it is confirmed through these studies that the superplasticizers not only affect the fresh state properties but also the hardened state properties of the cement paste.

CHAPTER 6

CEMENT-SUPERPLASTICIZER COMPATIBILITY

6.1 GENERAL

The influence of the type and dosage of superplasticizers on the flow behaviour of paste and concrete, as well as on the microstructure of the cement paste, has been discussed in the previous Chapters. In addition, the chemical composition of cement also plays an important role in the cement-superplasticizer interaction and the incompatibilities that can arise. An incompatibility can be defined as any undesirable effect that may be produced in the properties of concrete due to the particular combination of cement and superplasticizer. It is obvious that with a variety of cements and variability of their chemical compounds incompatible situations could arise. The literature reveals that cement-superplasticizer compatibility is affected by the following parameters related to the cement: chemical and phase composition, especially the C_3A content, alkali content, amount and type of calcium sulphate (gypsum, hemihydrates or anhydrite), cement fineness and free lime content (Hanehara and Yamada., 1999; Jiang et al., 1999; Yamada et al., 2001; Tagnit-Hamou et al., 2003).

The objective of this chapter is to understand the influence of the chemical composition of the cement on the cement-superplasticizer interaction and to suggest some guidelines for selecting the best combinations. Compatibility in terms of rheology and setting time is investigated for different types of cements with different superplasticizers. Also, an attempt is made through an adsorption study based on UV absorbance to understand the reason for the loss of fluidity and to explain why a higher dosage is required for some types of superplasticizers.

6.2 MATERIALS SELECTION AND CHARACTERISATION

6.2.1 Types of cements

To consider a reasonable number of material combinations, three commercial brands of cements were identified. Cement that had created some incompatibility problems in the laboratory trials was selected as the fourth one. The chemical analyses of these cements were done in National Test House, Chennai, and the physical properties were determined in the Construction Materials Laboratory of IITM. The chemical properties of selected cements are given in Table 6.1, along with its Bogue composition determined as per ASTM C 150 (2007a). The physical properties are given in Table 6.2. The important aspects of the four cements are given below.

Cement 1 (C1)

This cement has C_3S, C_2S and oxide contents in the normal range and a low C_3A content. The alkali and SO_3 contents are also within the allowable limits of 0.2-1.2% and 2-3.5%, respectively, of ordinary portland cement.

Cement 2 (C2)

It contains high C_2S and high insoluble residue but a low C_3S content. It has the highest SiO_2 content of the cements studied whereas the other oxides are within normal ranges. This cement has a low alkali content as the $(Na_2O)eq$ is 0.086%. Also, its fineness is higher compared to the other cements.

Cement 3 (C3)

CaO content and alumina/iron oxide ratio is higher for this cement compared to other cements. Other compounds are within the permissible limits.

Cement 4 (C4)

CaO and SO_3 are least for this cement whereas Al_2O_3 and MgO are highest, compared to the other cement studied. Loss on ignition is least for this cement whereas the insoluble residue is high. It has the highest C_3A content and also a high alkali content compared to other cements.

Table 6.1. Chemical and Bogue compositions of different cements

Analyte	Percentage of mass			
	C1	C2	C3	C4
CaO	60.81	61.14	62.13	59.44
SiO_2	19.5	22.95	20.84	21.04
Al_2O_3	4.12	4.62	4.88	5.67
Fe_2O_3	4.72	4.1	4.29	4.99
MgO	1.52	0.72	0.85	1.78
SO_3	2.48	2.48	1.69	1.39
L. O. I	3.41	3.61	3.47	1.97
Insoluble residue	1.51	2.98	1.41	3.3
Cl	0.01	0.02	0.03	0.03
Na_2O	0.05	0.04	0.18	0.22
K_2O	0.28	0.07	0.52	0.54
$(Na_2O)eq$	0.234	0.086	0.52	0.575
Lime saturation factor	0.93	0.82	0.91	0.86
Alumina/iron oxide ratio	0.68	1.13	1.14	1.136
C_3S	53.99	28.21	48.72	30.78
C_2S	15.18	44.51	22.99	37.10
C_3A	2.94	5.31	5.673	6.58
C_4AF	14.36	12.48	13.05	15.18

Table 6.2. Physical properties of different types of cements

Physical property	Quantity			
	C1	C2	C3	C4
Water demand for normal consistency of cement (%)	33	30	31	31
Initial setting time (minutes)	99	100	170	85
Final setting time (minutes)	184	220	290	215
Blaine specific surface area (m^2/kg)	316	371	355	301

6.2.2 Superplasticizers

Superplasticizers used in the present compatibility study with cements C2, C3 and C4 were selected from the work presented in Chapter 3 where only cement C1 was used. Four superplasticizers (a lignosulphonate, a melamine, a naphthalene and a polycarboxylate) all belonging to ASTM C 494 (2008a) type F and the fifth one belonging to Type G were selected; see Table 3.4 for the properties. Another naphthalene based superplasticizer (SNF-C2), which had created problems of slow setting, was also used along with C3 and C4; the properties of this admixture are: solid content of 40%, density of 1.2 kg/litre and pH of 7.5.

6.3 Experimental Procedure

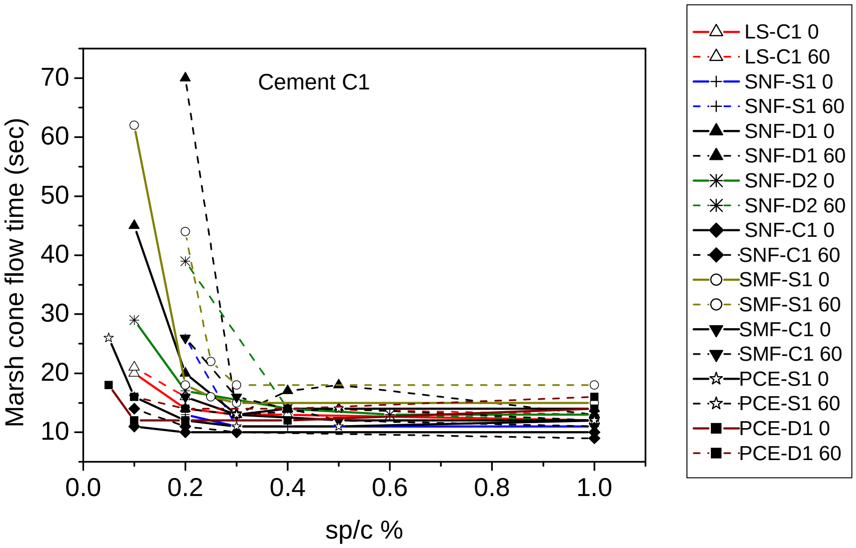
The mixing procedure for the preparation of cement paste was the same as given in Section 3.4. The pastes were tested at ambient temperature, in the range of 30-32°C. The tests conducted to understand the flow behaviour were the Marsh cone, mini-slump and viscometric tests. Marsh cone test was conducted to determine the saturation dosage of superplasticizer in each case, which is supported by mini-slump test results. The Bingham model was used to derive the yield stress and plastic viscosity of different compositions from viscometric test results. The setting of different combinations was studied with the Vicat apparatus.

6.4 Results and discussions

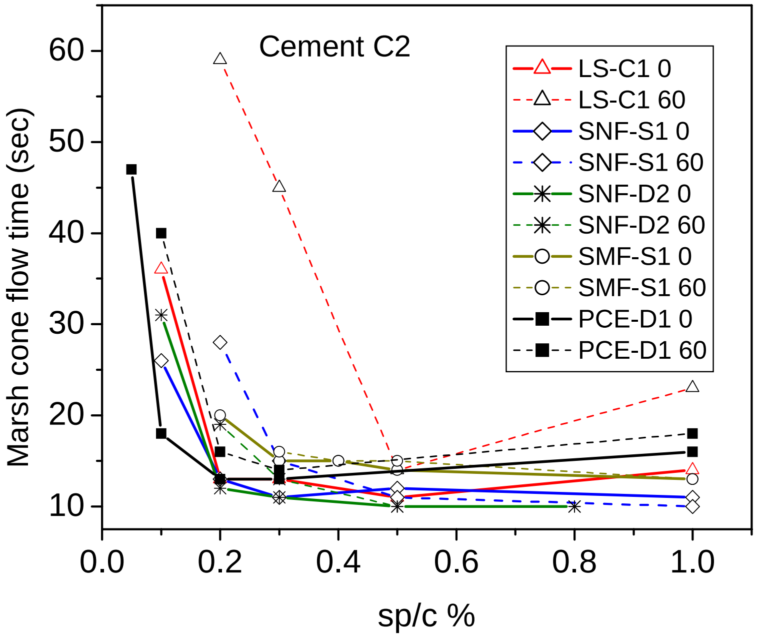
6.4.1 Influence of Cement Composition on the Flow Behaviour of Superplasticized Pastes

The flow behaviour of cement C1 with different types of superplasticizers has been discussed in detail already in Chapter 3; the Marsh cone flow time curves are reproduced in Figure 6.1(a) to provide comparisons with the behaviour obtained with other three cements that will be discussed here. The salient features of the behaviour of the pastes with the cement C1 are: (1) the saturation dosage of LS-C1 is slightly higher than those of the SNF and SMF based superplasticizers whereas the flow behaviour is comparable; (2) at very low dosages, SMF-S1 seems to give a high flow time, indicating the poorer dispersion of cement particles and lower fluidity; (3) the lower saturation dosage of 0.07% for PCE-D1 indicates that the combined mechanisms of electrostatic repulsion and steric hindrance makes it effective even at very low dosages; and (4) the flow time curves corresponding to 60 minutes are similar to those at 0-minutes for the saturation dosage and above (except for the case of the SMF-S1), indicating a negligible loss in fluidity beyond the saturation dosage, which reiterates the importance of using an appropriate dosage of superplasticizer for maintaining the fluidity for the required period.

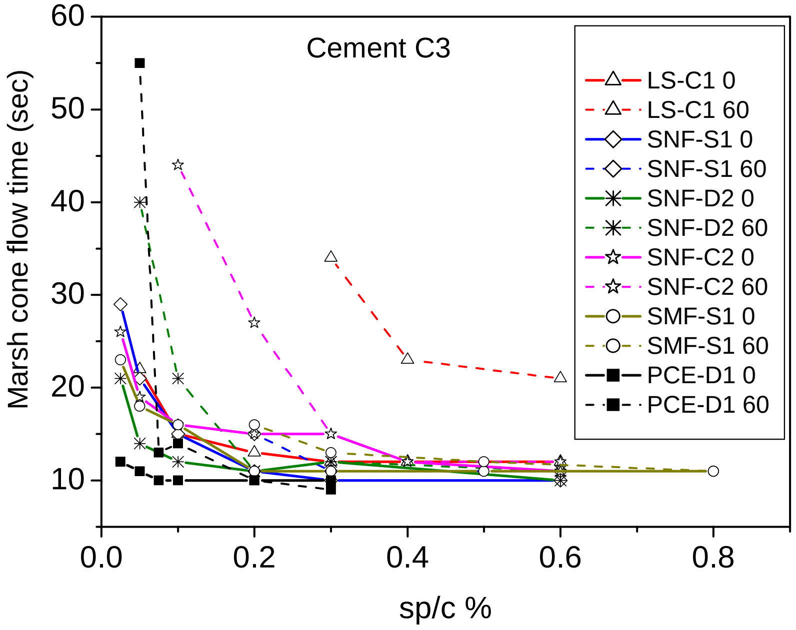
The Marsh cone flow time curves of 0 and 60 minutes for the other three cements C2, C3 and C4 are given in Figure 6.1 (b-d). In the case of cement C2, the saturation dosages are generally higher than those obtained with cement C1 and the loss of fluidity is high only in the paste with LS-C1. With cement C3, though the initial fluidity is in the same range as in the other cements for the studied combinations, there is generally a higher loss of fluidity, especially at dosages less than the saturation point. The loss of fluidity with cement C4 is even higher for all the studied combinations and severe at low superplasticizer dosage. This can be attributed to a high C_3A content in cement C4 (compared to cement C1).



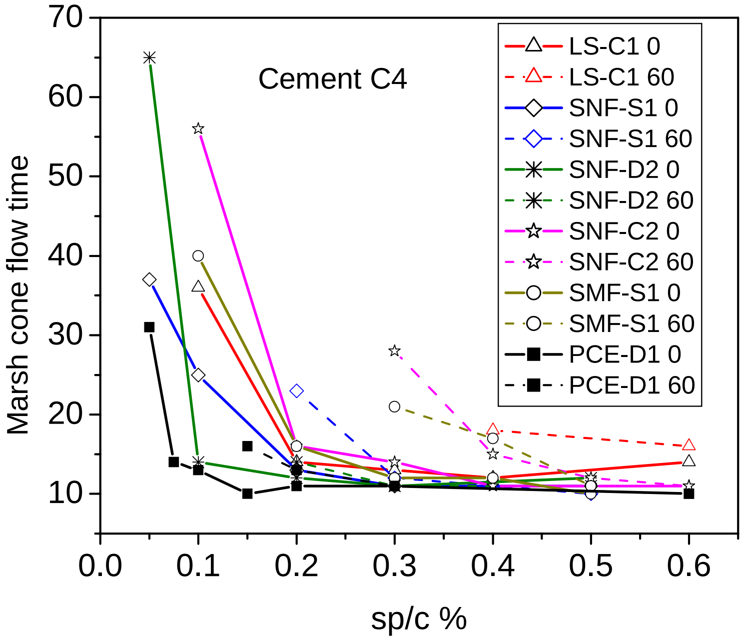
(a) Marsh cone flow time curves for Cement C1



(b) Marsh cone flow time curves for Cement C2



(c) Marsh cone flow time curves for Cement C3



(d) Marsh cone flow time curves for Cement C4

Fig. 6.1 Marsh cone flow times of different cement-superplasticizer combinations

The data from the Marsh cone, mini-slump and viscometer tests for the pastes with different superplasticizers at 0 and 60-minutes and all the four cements are given in Tables 6.3-6.6, respectively. The results show that the trends obtained are generally the same; i.e., the fluidity of the paste increases with an increase in the dosage of superplasticizer upto saturation dosage and remains practically constant after that.

The mini-slump spreads reflect the loss of fluidity at low superplasticizer dosages, as already discussed in the context of the Marsh cone flow times. Beyond the saturation dosage, the spread value at 60 minutes is almost the same as that obtained immediately after mixing. It was seen that pastes with mini-slump spreads of more than 165 mm exhibited bleeding. Also, some pastes that exhibited bleeding at 0 minutes improved in this aspect after 60 minutes due to the reduction in fluidity.

Table 6.3 Test data for pastes with different superplasticizers for cement C1

Type of sp	sp/c %	Flow time (sec)		Mini slump spread (mm)		Yield stress (Pa)		Plastic viscosity (Pa s)	
		0 min	60 min	0 min	60 min	0 min	60 min	0 min	60 min
LS-C1	0.1	20	21	93	90	12.20	13.50	0.122	0.132
	0.2	14	16	153	123	5.81	7.59	0.089	0.097
	0.3	13	13	162	143	2.0	3.15	0.059	0.075
	0.4	13	14	163	163	1.0	0.35	0.050	0.064
	1	12	13	164	162	0.5	0.23	0.068	0.049
SNF-S1	0.2	13	26	143	90	16.21	24.61	0.143	0.185
	0.3	11	11	151	150	1.80	5.91	0.055	0.066
	0.4	11	11	165	163	0.0	0.21	0.033	0.054
	1	11	11	170	178	0.09	0.10	0.031	0.025
SNF-D1	0.1	45	*	82	*	18.31	20.23	0.197	0.241
	0.2	20	70	96	*	12.13	16.61	0.139	0.178
	0.3	13	13	127	115	2.88	5.98	0.074	0.089
	0.4	14	17	bleeding	141	0.08	0.09	0.049	0.083
	0.5	14	18	bleeding	164	0.11	0	0.043	0.045
	1	14	13	bleeding	163	0.09	0.12	0.033	0.035
SNF- D2	0.1	29	*	87	*	16.99	25.52	0.197	0.194
	0.2	17	39	106	87	6.94	12.10	0.088	0.149
	0.4	14	14	bleeding	148	0.55	0	0.042	0.043
	0.6	13	13	bleeding	176	0.37	0.25	0.041	0.039
	1	13	12	bleeding	160	0.13	0.07	0.045	0.038
SNF-C1	0.1	11	14	126	95	6.72	7.24	0.057	0.046
	0.2	10	11	152	128	1.25	6.69	0.042	0.064
	0.3	10	10	168	168	0.72	0.77	0.029	0.046
	1	10	9	173	178	0.24	0.17	0.023	0.035
SMF-S1	0.1	62	*		*	20.39	*	0.177	*
	0.2	18	44	102	90	6.89	2.39	0.076	0.092
	0.25	16	22	115	109	2.36	3.77	0.098	0.101
	0.3	15	18	122	113	1.54	8.97	0.078	0.065
	1	15	18	167	161	0.77	0	0.048	0.043
SMF-C1	0.1	>120	*	*	*	33.14	*	0.199	*
	0.2	16	26	108	103	13.44	30.92	0.128	0.139
	0.3	13	16	132	112	2.88	7.71	0.074	0.100
	0.5	12	12	181	169	0	0	0.039	0.042
	1	12	11	177	172	0	0	0.037	0.041
PCE-S1	0.05	26	*	86.3	*	17.55	*	0.155	*
	0.1	16	*	110	*	11.07	23.67	0.089	0.162
	0.2	12	14	bleeding	157	0.51	0.36	0.073	0.068
	0.3	11	13	bleeding	179	0	0.08	0.034	
	0.5	11	14	bleeding	192	0	0	*	0.035
	1	12	12	bleeding	bleeding	0		0.034	0.034
PCE-D1	0.05	18	*	97	*	24.45	*	0.214	*
	0.1	12	16	166	147	0.01	2.37	0.035	0.079
	0.2	12	14	170	bleeding	0	0.09	0.035	0.043
	0.4	12	14	199	bleeding	0	0	0.036	0.036
	1	14	16	193	bleeding	0	0	0.047	0.054

From the data of the viscometer tests, it can be seen that in general the yield stress decreases significantly with an increase in the dosage of superplasticizer down to a value of practically zero beyond the saturation dosage. The plastic viscosity also reduces with an increase in the superplasticizer dosage. It is observed that the yield stress and plastic viscosity developed vary from 0-43 Pa and 0.034-0.188 Pa.s, respectively. Both the rheological parameters increase with time as seen in the comparison of the 0 and 60 minute data.

Table 6.4 Test data for pastes with different superplasticizers for cement C2

Type of sp	sp/c %	Flow time (sec)		Mini slump spread (mm)		Yield stress (Pa)		Plastic viscosity (Pa s)	
		0 min	60 min	0 min	60 min	0 min	60 min	0 min	60 min
LS-C1	0.1	36	*	85	*	33.45	*	0.185	*
	0.2	13	59	123	90	15.33	24.34	0.095	0.142
	0.3	13	45	140	113	7.72	12.99	0.086	0.113
	0.5	11	14	bleeding	143	0.26	3.61	0.047	0.090
	1	14	23	bleeding	120	0.24	1.28	0.068	0.130
SNF-S1	0.1	26	*	84	*	38.16	*	0.162	*
	0.2	13	28	125	89	11.64	1.83	0.095	0.076
	0.3	11	15	bleeding	138	1.2	3.04	0.073	0.073
	0.5	12	11	bleeding	bleeding	0.19	0.32	0.040	0.034
	1	11	10	bleeding	bleeding	0.31	0.13	0.043	0.043
SNF-D2	0.1	31	*	85	*	22.56	*	0.170	*
	0.2	12	19	130	113	6.78	26.27	0.074	0.181
	0.3	11	13	153	143	0.44	3.85	0.057	0.073
	0.5	10	10	bleeding	bleeding	0	0.014	0.043	0.039
	0.8	10	10	bleeding	bleeding	0	0	0.038	0.046
SMF-S1	0.1	*	*	*	*	*	*	*	*
	0.2	20	*	85	*	20.73	34.26	0.123	0.188
	0.3	15	16	148	145	13.13	12.32	0.090	0.053
	0.4	15	15	149	150	1.65	3.72	0.083	0.078
	0.5	14	15	153	148	0.70	1.15	0.084	0.082
	1	13	13	bleeding	bleeding	0.04	0	0.052	0.052
PCE-D1	0.05	47	*	75	*	42.97	*	0.165	*
	0.1	18	40	115	85	13.39	23.98	0.110	0.143
	0.2	13	16	145	153	0.51	0.80	0.087	0.102
	0.3	13	14	155	163	0.42	0.36	0.074	0.074
	1	16	18	158	148	0.32	0.56	0.086	0.092

Table 6.5 Test data for pastes with different superplasticizers for cement C3

Type of sp	sp/c %	Flow time (sec)		Mini slump spread (mm)		Yield stress (Pa)		Plastic viscosity (Pa s)	
		0 min	60 min	0 min	60 min	0 min	60 min	0 min	60 min
LS-C1	0.05	22	*	83	*	14.99	*	0.163	*
	0.1	15	*	102	74	13.98	17.33	0.119	0.112
	0.2	13	*	128	77	11.39	21.82	0.099	0.147
	0.3	12	34	145	91	4.07	15.74	0.072	0.122
	0.4	12	23	bleeding	108	0.29	12.70	0.056	0.100
	0.6	12	21	bleeding	148	0.067	2.11	0.019	0.103
SNF-S1	0.025	29	*	97	75	16.10	21.78	0.152	0.197
	0.05	21	*	100	85	15.84	25.34	0.169	0.145
	0.1	15	*	107	85	14.26	19.04	0.109	0.182
	0.2	11	15	139	118	3.21	12.16	0.061	0.109
	0.3	10	11	bleeding	154	0.59	0.53	0.043	0.054
	0.6	10	11	bleeding		0	0.62	0.029	0.084
SNF-D2	0.025	21	*	85	76	3.189	22.91	0.086	0.168
	0.05	14	40	108	85	13.272	15.93	0.113	0.135
	0.1	12	21	125	108	7.573	14.95	0.058	0.124
	0.2	11	11	140	148	1.023	0.76	0.036	0.065
	0.3	12	12	bleeding	165	0	1.61	0.048	0.289
	0.6	10	11	bleeding	170	0	0	0.033	0.021
SNF-C2	0.025	26	*	93	*	16.02	*	0.138	*
	0.05	19	*	-	78	15.68	18.39	0.145	0.182
	0.1	16	44	-	79	9.61	18.65	0.079	0.176
	0.2	15	27	108	83	7.75	16.05	0.073	0.137
	0.3	15	15	144	108	3.22	5.02	0.048	0.065
	0.4	12	12	bleeding	190	0	0	0.019	0.042
	0.6	11	12	bleeding	bleeding	0	0	0.016	0.012
SMF-S1	0.025	23	*	98	*	17.59	21.75	0.17	0.217
	0.05	18	*	93	*	14.60	20.42	0.126	0.179
	0.1	16	*	103	73	14.31	*	0.122	*
	0.2	11	16	128	103	5.30	9.63	0.071	0.069
	0.3	11	13	141	115	1.53	5.46	0.056	0.073
	0.5	11	12	bleeding	bleeding	0.72	0.15	0.043	0.039
	0.8	11	11	bleeding	bleeding	0	0	0.03	0.031
PCE-D1	0.025	12	*	130	*	6.78	*	0.077	*
	0.05	11	55	135	85	9.45	17.02	0.056	0.116
	0.075	10	13	bleeding	130	1.44	3.87	0.039	0.071
	0.1	10	14	bleeding	120	1.12	4.38	0.035	0.094
	0.2	10	10	*	168	0	-	0.030	-
	0.3	10	9	bleeding	175	0	0.12	0.032	0.0096

Table 6.6 Test data for pastes with different superplasticizers for cement C4

Type of sp	sp/c %	Flow time (sec)		Mini slump spread (mm)		Yield stress (Pa)		Plastic viscosity (Pa s)	
		0 min	60 min	0 min	60 min	0 min	60 min	0 min	60 min
LS-C1	0.1	36	*	78	*	*	*	*	*
	0.2	14	*	105	*	22.83	*	0.144	*
	0.3	13	*	125	*	10.36	*	0.088	*
	0.4	12	18	165	100	2.59	*	0.073	*
	0.6	14	16	bleeding	bleeding	0.30	0.1	0.047	0.054
SNF-S1	0.05	37	*	88	*	24.81	*	0.221	*
	0.1	25	*	86	*	22.26	*	0.188	*
	0.2	13	23	130	106	5.42	17.40	0.072	0.137
	0.3	11	12	bleeding	146	0.15	1.07	0.038	0.044
	0.5	11	10	bleeding	168	0	0	0.026	0.026
SNF-D2	0.05	65		86	*	29.59	*	0.264	*
	0.1	14	>84	118	83	10.95	22.60	0.095	0.238
	0.2	12	14	158	124	0.37	2.71	0.045	0.071
	0.3	11	11	178	160	0	0.0029	0.034	0.055
	0.5	12	11	bleeding	bleeding	0	0	0.031	0.026
SNF-C2	0.1	56	*	81	*	33.21	*	0.209	*
	0.2	16	*	101	83	21.80	37.50	0.159	0.261
	0.3	14	28	114	85	10.31	22.73	0.082	0.156
	0.4	11	15	bleeding	123	1.129	9.21	0.063	0.071
	0.5	11	12	bleeding	bleeding	0	0.16	0.051	0.037
	0.6	11	11	bleeding	165	0	0	0.043	0.037
SMF-S1	0.1	40	*	87	*	35.41	*	0.304	*
	0.2	16	*	107	*	20.69	*	0.185	*
	0.3	12	21	139	91	3.99	22.03	0.072	0.182
	0.4	12	17	145	105	4.04	9.29	0.078	0.087
	0.5	10	11	bleeding	168	0.24	0.09	0.052	0.040
PCE-D1	0.05	31	*	83	*	*	*	*	*
	0.075	14	*	112	*	28.25	*	0.132	*
	0.1	13	*	123	*	13.33	*	0.079	*
	0.15	10	16	bleeding	111	0.21	7.48	0.044	0.102
	0.2	11	13	bleeding	bleeding	0.09	0	0.034	0.06
	0.3	11	11	178	bleeding	0.03	0	0.025	0.035
	0.6	10	10	188	184	0	0	0.026	-

* could not be determined

Table 6.7 gives a comparison of the saturation dosages for the four cements obtained from Marsh cone flow curves at 0 minutes, using the same method as given in Chapter 3. It is observed that the saturation dosages of the LS, SMF and PCE based superplasticizers are generally the highest for the cement C2, mainly because it has comparatively higher surface area and hence the amount of superplasticizer needed is higher, which is in accordance with the reported results (Erdogdu, 2000). Also, it is a low alkali cement and therefore is expected to adsorb more superplasticizer (Dodson and Hayden, 1989; Jiang et al., 1999)

Table 6.7 Comparison of the saturation dosages at 0-minutes for different cements

Type of superplasticizer	Saturation dosages%			
	C1	C2	C3	C4
LS-C1	0.25	0.40	0.25	0.4
SNF-S1	0.20	0.25	0.20	0.25
SNF-D1	0.24	*	*	*
SNF-D2	0.23	0.3	0.2	0.2
SNF-C1	0.16	*	*	*
SNF-C2	*	*	0.2	0.4
SMF-S1	0.23	0.4	0.2	0.3
SMF-C1	0.20	*	*	*
PCE-S1	0.2	*	*	*
PCE-D1	0.07	0.2	0.08	0.15

Cement C3 gives good fluidity even at very low dosages and the saturation dosages obtained are comparatively lower for the various superplasticizers. The yield stress and plastic viscosity values are lower compared to those of pastes with other cements. However, some pastes with cement C3 do show a loss of fluidity within 60 minutes.

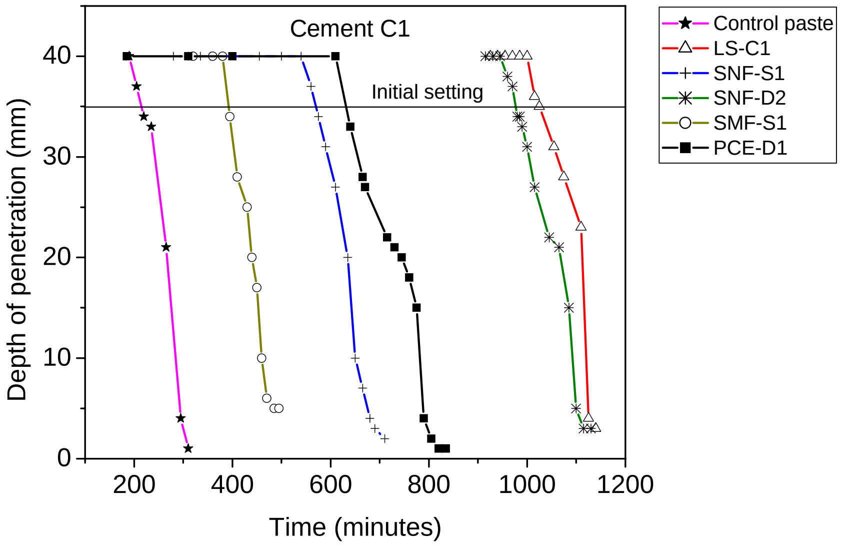
All combinations with cement C4 had rapid slump losses within 60 minutes and the saturation dosages of SNF-C2, PCE-D1 and LS-C1 were high. This may be due to the high C_3A content, which causes some of the superplasticizer to be absorbed by the initial hydration products of C_3A and hence less would be available in the solution for further adsorption. Also, cement C4 has a low SO_3 content and hence the SO_4^{2-} ions in the superplasticizer will compete with the sulphate ions of the cement, causing more initial adsorption, resulting in the increase of the superplasticizer demand.

The results reported by Kumar (2006) on the compatibility of concrete using cement C1 and C2 and different superplasticizers used here generally support the results of the present study; he found that the superplasticizers SMF-S1, SNF-S1 and PCE-D1 in combination with cement C1 gave better slump retention in concrete, even at low superplasticizer dosages, compared to the concretes with cement C2. As an extension of the previous study, Das (2007) conducted tests to study the compatibility of cements C3 and C4 and the same superplasticizers. His results also show that concretes with cement C4 had more slump loss than those with cement C3, as reported in the present study.

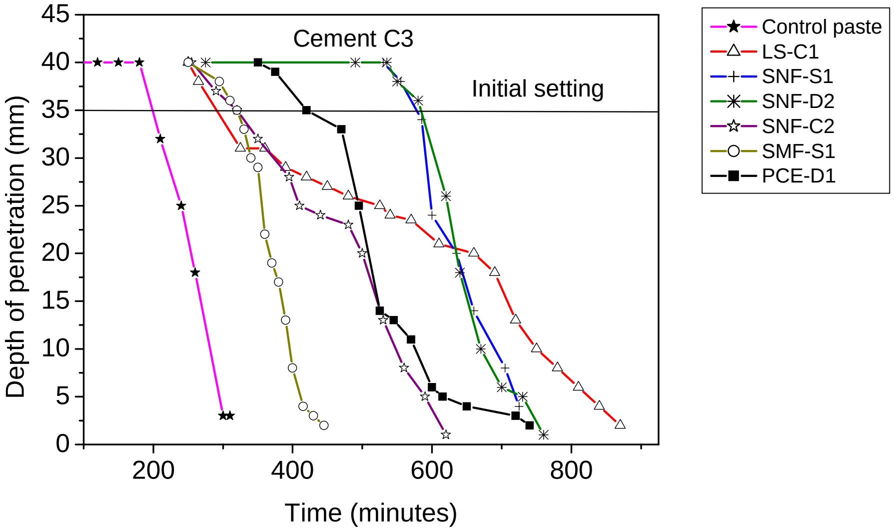
6.4.2 Influence of Cement Composition on the Setting of Superplasticized Pastes

The setting time is affected by both the chemical composition of cement, as well as by the type of superplasticizer, as seen in Figure 6.2 (a-c). It is seen that the trend of setting varies among the cements studied. It can be observed that for cement C1 and C3, the lowest retardation is seen for SMF-S1 but not in C4. For cement C4, LS-C1 and SNF-D2 superplasticizers gave the least retardation compared to other superplasticizers with the same cement. This is in sharp contrast to the behaviour of LS-C1 and SNF-D2 in the other cements, where it leads to high retardation. The mix with cement C4 and admixture SNF-C2 does not set even after 24 hours whereas the paste with cement C3 and the same admixture sets in about 10 hours.

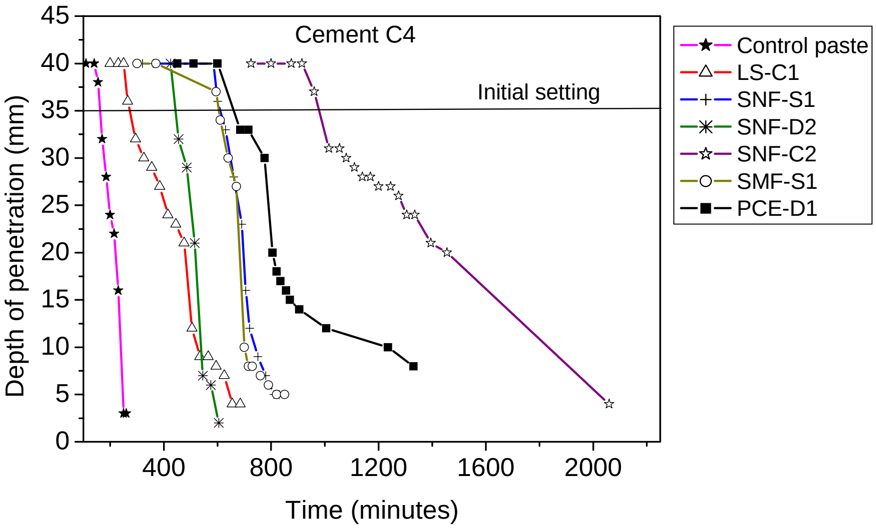
It can be seen that the setting behaviour can vary significantly depending on the cement composition and the superplasticizer used. Some of the trends cannot be explained on the basis of the literature or the data obtained in this work, and call for further research to provide the understanding needed.



(a) Vicat penetration test results of Cement C1



(b) Vicat penetration test results of Cement C3



(c) Vicat penetration test results of Cement C4

Fig. 6.2 Influence of type of cement on setting

The results of Kumar (2006) on setting with cement C1 shows the same trend as observed in the present paste study; the SNF-S1 gives lower setting time than PCE and SNF-D2 based superplasticized paste. The results of Das (2007) on setting are also comparable with the present results; he showed that concrete with the superplasticizer SNF-S1 exhibited higher setting time with cement C4 whereas SNF-D2 had a lower setting time, when compared with identical concretes with the cement C3.

6.5 STUDY OF THE ADSORPTION OF SUPERPLASTICIZERS

6.5.1 Background

As discussed earlier, the superplasticizer is adsorbed on the cement surface; the rate and amount of this adsorption varies with type of cement and superplasticizer, which in turn affects the fresh state properties of concrete. Consequently, adsorption plays an important role in the initial flow behaviour, the maintenance of fluidity as well as the setting behaviour of pastes. Hence an understanding of adsorption of different superplasticizers on different types of cement is required for answering several questions like why some superplasticizers that have good initial fluidity can not maintain it even for 60-minutes. Also, it could explain the variation in saturation dosage of the same superplasticizer for different types of cements.

The increase in workability due to the addition of superplasticizers occurs through the dispersion of agglomerated cement particles. However, the quantification of this mechanism is a difficult task and is further complicated by the hydration reactions. The adsorbed superplasticizer causes fluidity and the superplasticizer that is remaining in solution is responsible for fluidity retention, as explained in Chapter 2. UV absorbance techniques have been used to understand the amount of adsorption by several researchers, who have concluded that the method is highly precise and the results obtained are reproducible (Daimon and Roy, 1978, Andersen et al., 1987, Krishna, 1996, Kim et al., 2000).

In the present study, the adsorption behaviour of four families of superplasticizers and its relation to the fluidity of cement paste has been investigated at the saturation dosage of superplasticizer using UV absorbance technique.

6.5.2 Materials used

Superplasticizers belonging to the four families of products, namely lignosulphonates (LS), melamines (SMF), naphthalenes (SNF) and polycarboxylates (PCE), were used. The details of the superplasticizers are given in Table 3.4. OPC 53 grade cements C1, C2,C3 and C4, with the characteristics given in Table 6.1, were used in the study.

6.5.3 Experimental Procedure

The concentration of polymer in the liquid phase was determined through a quantification of the UV absorbance using a JASCO V-570 UV spectrophotometer in the 190-400 nm region. According to the Beer-Lambert's law, the absorbance is directly proportional to the concentration of the absorbing material in solution. In absorption spectroscopy, the intensity of light of a particular wavelength that is absorbed by the sample is measured and used to determine the absorbance using the following equations:

$$A = \log_{10} \frac{I_0}{I_1} \tag{6.1}$$

where A is the absorbance, $A = \alpha\ l\ c$ (6.2)

α is the absorption coefficient, l is the distance that the light travels through the material, c is the concentration of the absorbing species in the material, I_0 is the intensity of incident light, and I_1 is the intensity after passing through the material.

UV spectrometry is used here for the measurement of the absorbance of different superplasticizers. The test procedure is as follows.

Step 1: Determination of the characteristic peak wavelength (λ_{max}) of the superplasticizer

The first step in the method is to determine the wavelength corresponding to maximum absorbance for a particular superplasticizer; absorbance measurements made at that wavelength are expected to have the least errors. 0.1 ml of a solution of water and superplasticizer, with a known superplasticizer concentration, is taken and further diluted as 250X, 500X, 1000X, 10000X, etc. Water, used as the reference liquid for the measurements, was placed in another couette along with the diluted sample in the UV-visible spectrometer. Measurements are made for each of the diluted solutions until an absorbance peak is obtained within the measurable range of the instrument (maximum of 5 for the equipment used here). The UV spectra for the different superplasticizers are shown in Figure 6.3, showing different peak absorbance values and the corresponding wavelengths (denoted as λ_{max}). Note that the dilutions are different in all the cases so that absorbance values are not directly comparable. It is observed that the λ_{max} is 205 nm for LS-C1, 215 nm for SMF-S1, 225 nm for SNF-S1 and 195nm for PCE-D1. The absorbance by the superplasticizer in the aqueous solution was determined hereafter at the corresponding λ_{max}.

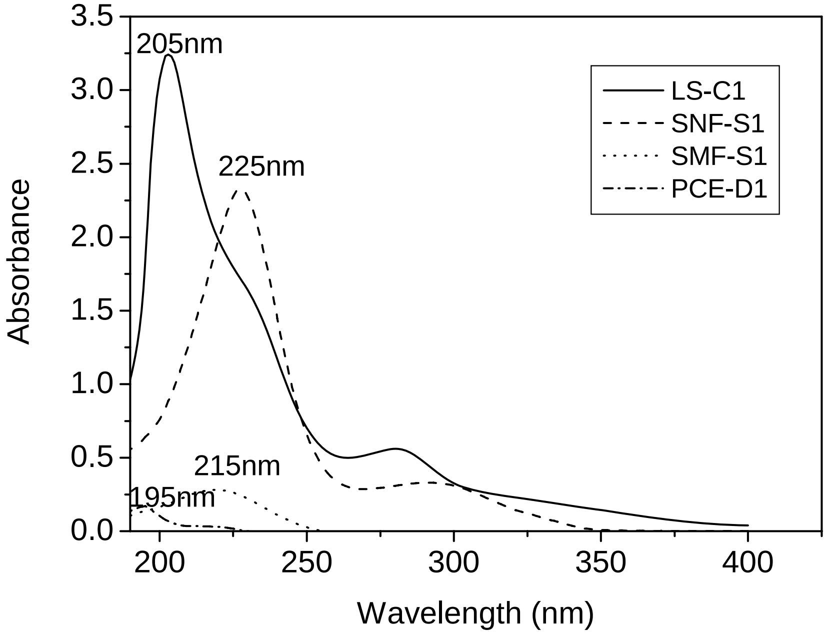


Fig. 6.3 Absorbance spectra for different superplasticizers

Step 2: Determination of the absorbance of the superplasticizers in cement paste

The cement pastes were prepared with the saturation dosage of superplasticizer. The aqueous solution was extracted by centrifuging the paste at 6000 rpm for 10 minutes. The extracted solution was diluted with deionized water to obtain a solution with an absorbance in the measureable range. The absorbance spectrum is obtained and the peak absorbance was noted for the corresponding wavelength, as explained in step 1.

6.5.4 Results and discussion of absorbance tests

The absorbance spectrum of the aqueous solution extracted from the paste with cement C1 and lignosulphonate based superplasticizer just after mixing is given in

Figure 6.4. The comparison of the same with Fig. 6.3 shows that peak absorbance for this superplasticizer occurs at the same wavelength of 205 nm for both the solution in water and the aqueous solution extracted from the cement paste. It is also seen that there is no other peak in the spectrum, which indicates that there is no other species in the aqueous solution of the paste with significant absorbance other than the superplasticizer. The same is true for all the other superplasticizers, as seen in the other plots of Figure. 6.4.

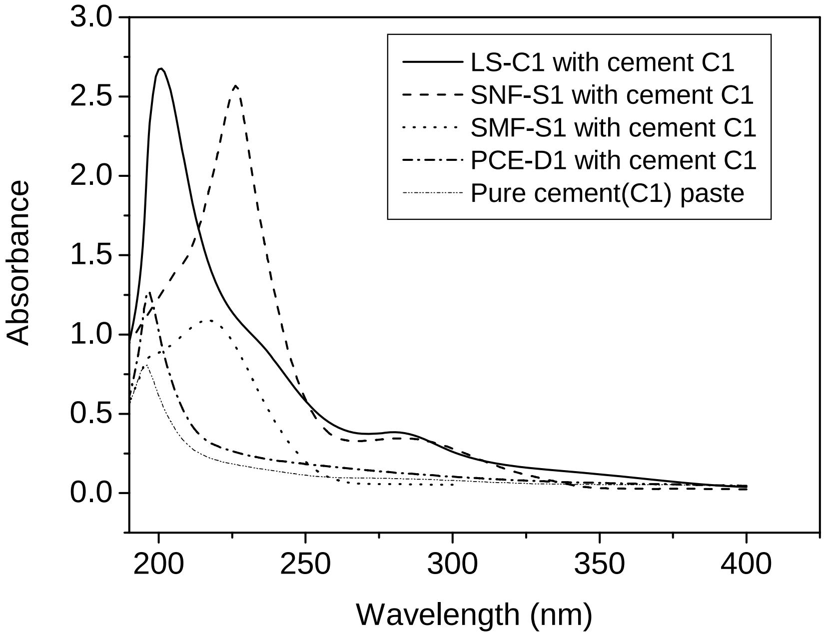


Fig. 6.4 Absorbance spectrum of the diluted aqueous solutions of superplasticized pastes extracted after mixing

The absorbance spectrum of the solution extracted from the pure cement paste is also given in the same graph. Note that each of the curves is for a different dilution and are not, therefore, directly comparable; the dilutions for the corresponding aqueous solutions are: LS-C1: 250X (i.e., 0.1 ml of the aqueous solution is diluted in 25 ml of water), SNF-S1: 500X, SMF-S1: 1000X and PCE-D1: 250X. The absorbance spectra of the superplasticized cement pastes at 90 minutes were also obtained in the same manner. Note that the age of the aqueous solution at the time of the measurements is estimated as 15 minutes.

The absorbance values for tests at 15-minutes and 90-minutes for the different superplasticizers in combination with cement C1 are summarized in Table 6.8. The absorbance at the saturation dosage for different pastes depends on both the family of superplasticizer and chemical composition of cement. The absorbance of SNF-S1 and SMF-S1 is lower at 90-minutes compared to that at 15-minutes showing that the adsorption of the superplasticizer has increased with time. In the other cases, the absorbance is almost the same at both 15 and 90 minutes indicating that the adsorption of those superplasticizers does not increase over this time range. It should be noted that the presence of cement particles in the aqueous solution and the possible desorption of the superplasticizer from these fine particles during subsequent dilution process could distort the absorbance values by giving falsely high values that could be attributed to the unadsorbed admixtures (Daimon and Roy, 1978). This is a major limitation of the procedure and further studies are needed to get a better estimate of the amount of adsorbed superplasticizer on the cement particles and its evolution with time.

Table 6.8 Summary of absorbance test results

Combination	Dilution		Absorbance	
	15 minutes	90 minutes	15 minutes	90 minutes
Cement C1+LS-C1	250X	250X	2.7	2.9
Cement C1+SNF-D1	500X	500X	2.6	1.9
Cement C1+SMF-S1	1000X	1000X	1.1	0.8
Cement C1+PCE-D1	250X	250X	1.3	2.1
Cement C1 +PCE-D1 (0.05%)	250X	250X	1.1	1.2
Cement C2 +LS-C1	250X	250X	2.2	2.0
Cement C2+PCE-D1	250X	250X	0.4	0.4
Cement C4+PCE-D1	250X	250X	1.3	1.0

6.5.4.1 Variation in Superplasticizer Absorbance with Type of Cement

The absorbance for the pastes with cement C2 and LS-C1 is less than that with cement C1 and LS-C1 for the same dilution (see Figure 6.5). This suggests that the initial adsorption may be more in the case of the paste with cement C2 and LS-C1 than in the paste with cement C1 and LS-C1, resulting in the higher loss of fluidity, as described earlier. This could be attributed to the higher surface area of cement C2 and its low alkali content, both of which can increase the adsorption. Similarly, for the paste with cement C2 and the PCE, the absorbance at 15 and 90-minutes is low compared to the C1-PCE-D1 combination, supporting the results shown earlier where there is more loss of fluidity and higher superplasticizer demand in the former.

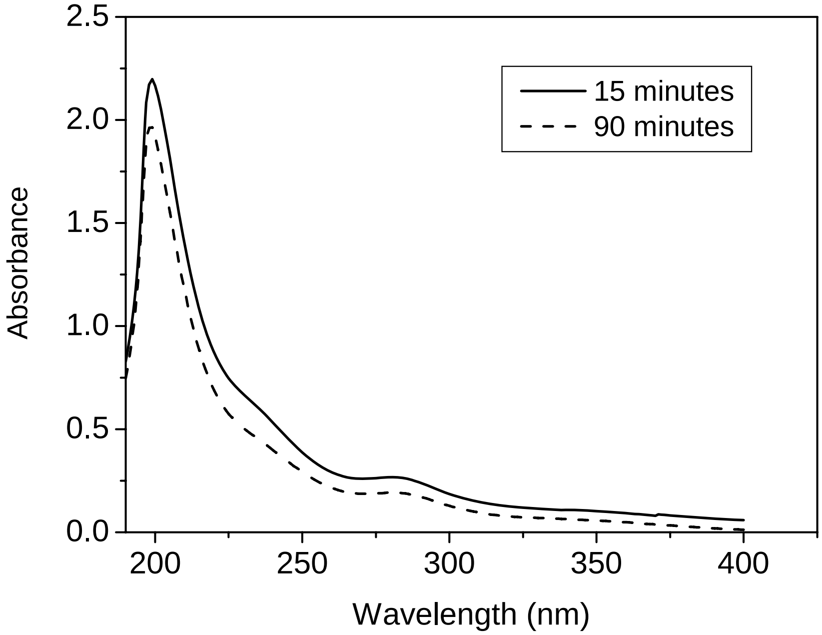


Fig. 6.5 Absorbance spectra for cement C2 and LS-C1

6.6 IDENTIFYING COMPATIBLE CEMENT-SUPERPLASTICIZER COMBINATIONS

As indicated in the preceding chapters, a number of mechanisms and interactions can contribute to the so-called incompatibility between the cement and superplasticizer. All of these mechanisms are complex and interrelated. The results show that a single test is not sufficient to determine a compatible cement-superplasticizer combination. Consequently, a simple methodology that combines different test procedures is developed based to select the compatible combinations.

A flow chart representing the methodology for the selection of an appropriate cement-superplasticizer combination based on the present interaction study is shown in Figure 6.6. The entire methodology is divided into two steps; the method of selection of a compatible combination of cement and superplasticizer from the paste studies is described in step 1. Step 2 describes the methodology for the final selection of cement-superplasticizer combination based on workability, strength and cost by conducting trial tests on concrete.

Step 1

- The water demand and setting time of cement, and the density, solid content and pH of superplasticizer are to be determined for recording the basic properties for the quality checks, as well as for comparing different batches of products.
- The Hobart mixer or a similar intensive mixer is considered to be essential for the preparation of paste for selecting a compatible combination based on the paste studies as well as for correlating with concrete results.
- The first criterion in the selection process is based on the ability to obtain a well-defined saturation dosage from the Marsh cone test that is within the maximum dosage of the superplasticizer as recommended by the supplier. The study of the flow behaviour of superplasticized paste has shown that results from the mini-slump and viscometer tests can be correlated with those of the Marsh cone test results and, therefore, need not be carried out since they

require more sophisticated equipment or may not be as sensitive. The correlation between the flow behaviour of paste, mortar and concrete has shown that the dosage obtained from the paste tests can be used as the guideline for selecting the dosage of superplasticizer for concrete.

- As seen from the studies on the loss of flow and UV absorbance, the flow behaviour can vary significantly with time in the fresh paste. Therefore, it is recommended that the saturation dosage be obtained at the age that corresponds to the actual initiation of the placing of concrete (e.g., age when the concrete is expected to be delivered to the site, in the case of ready-mixed concrete).
- The influence of superplasticizer on the setting behaviour of the paste is the second criterion for compatibility. Here, the final setting time is limited to 16 hours as obtained in the Vicat penetration test, unless there is deliberate retardation through the use of a retarder or a superplasticizer with retarding properties. The results of the study suggest that if this criterion is satisfied, the FST of concrete would be not more than 12 hours since the difference between the FSTs of paste and concrete was found to be normally not more than 4 hours. Since the electrical resistivity measurements require more technical expertise than the Vicat penetration apparatus and there is only limited experience with such tests, it is deemed to be unnecessary for determining the compatibility. In any case, the IST obtained with Vicat apparatus correlates well with the dormant stage extension obtained from electrical resistivity measurements.
- The microstructural analysis is not included in the methodology since the studies previously discussed show that a paste with adequate workability and normal setting behaviour generally has a uniform microstructure.

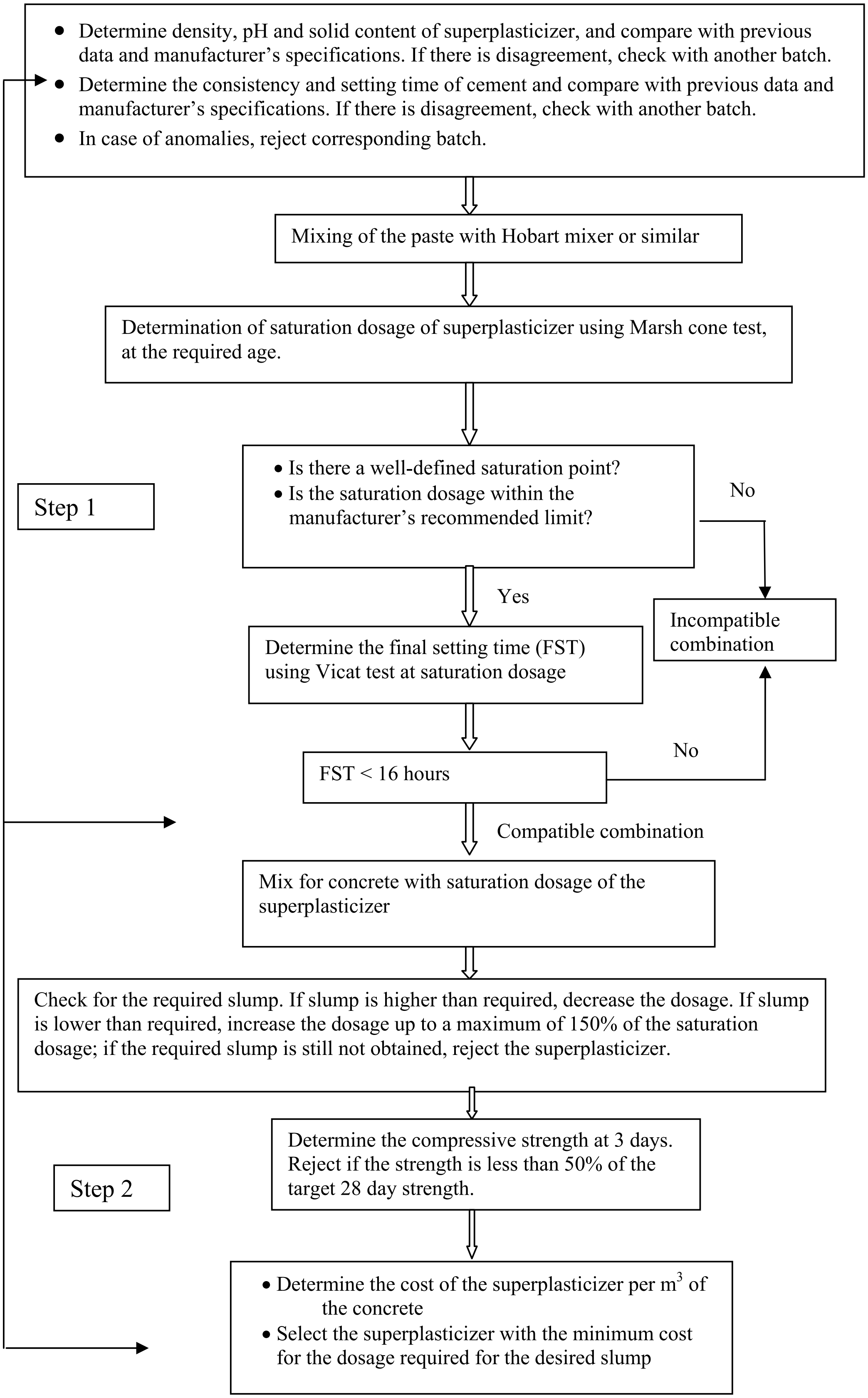
Step 2

- Final trials are done on concrete, within this selection procedure, to complement the paste tests and, more importantly, to ensure a mix with the required slump and compressive strength. It is assumed that the paste volume and the aggregate skeleton are optimized independently, for example with a method based on packing density or other, as in the methods of Toralles-Carbonari et al. (1996) and Gomes et al. (2001).

- The study has shown that the fines content in the aggregates can increase the superplasticizer demand to more than the saturation dosage of the superplasticizer, which also supports the necessity for the final trials on concrete. In such cases, a higher dosage than the saturation point may be used for achieving the desired workability; however, it is recommended that the dosage is not more than 150% of the saturation dosage in order to limit the retardation and possible segregation, as well as cost. Obviously, the superplasticizer dosage can be reduced if the slump obtained is more than the desired value when the saturation dosage is used.

- From the point of view of productivity, a minimum value of 50% of the 28-day compressive strength is recommended at 3 days. This criterion can be waived when the early age strength is not critical.

- The final choice of the superplasticizer can be based on the minimum cost considering the dosage of the superplasticizer for obtaining the desired slump among the compatible combinations. Superplasticizers can also be short-listed for further testing based on tests on pastes, for example, by comparing flow times and saturation dosages.



- Determine density, pH and solid content of superplasticizer, and compare with previous data and manufacturer's specifications. If there is disagreement, check with another batch.
- Determine the consistency and setting time of cement and compare with previous data and manufacturer's specifications. If there is disagreement, check with another batch.
- In case of anomalies, reject corresponding batch.

Mixing of the paste with Hobart mixer or similar

Determination of saturation dosage of superplasticizer using Marsh cone test, at the required age.

- Is there a well-defined saturation point?
- Is the saturation dosage within the manufacturer's recommended limit?

Determine the final setting time (FST) using Vicat test at saturation dosage

FST < 16 hours

Mix for concrete with saturation dosage of the superplasticizer

Check for the required slump. If slump is higher than required, decrease the dosage. If slump is lower than required, increase the dosage up to a maximum of 150% of the saturation dosage; if the required slump is still not obtained, reject the superplasticizer.

Determine the compressive strength at 3 days. Reject if the strength is less than 50% of the target 28 day strength.

- Determine the cost of the superplasticizer per m^3 of the concrete
- Select the superplasticizer with the minimum cost for the dosage required for the desired slump

Fig. 6.6 Methodology to select the Compatible Cement-Superplasticizer Combination

The summary of the paste test results along with the compatibility criteria derived from the methodology for different combinations at 0-minutes and 60-minutes are given in Tables 6.9 and 6.10, respectively. The nomenclature used for the mixes is as follows; the first letter represents the type of cement followed by the admixture code, e.g.,C1/LS-C1 is the mix with cement C1 and superplasticizer, LS-C1.

Table 6.9 Summary of Superplasticized paste combinations at 0-minutes

Mix compositions	Saturation dosage within the manufacturer's recommended limit at 0 min	Final Setting ≤ 16 hr	Compatible?
C1/LS-C1	Yes	Yes	Yes
C1/SNF-S1	Yes	Yes	Yes
C1/SNF-D1	Yes	Yes	Yes
C1/SNF-D2	Yes	Yes	Yes
C1/SNF-C1	Yes	Yes	Yes
C1/SMF-S1	Yes	Yes	Yes
C1/SMF-C1	Yes	Yes	Yes
C1/PCE S1	Yes	Yes	Yes
C1/PCE-D1	Yes	Yes	Yes
C2/LS-C1	**No**	*****	**No**
C2/SNF-S1	Yes	*	Yes
C2/SNF-D2	Yes	*	Yes
C2/SMF-S1	Yes	*	Yes
C2/PCE-D1	Yes	*	Yes
C3/LS-C1	Yes	Yes	Yes
C3/SNF-S1	Yes	Yes	Yes
C3/SNF-D2	Yes	Yes	Yes
C3/SNF-C2	Yes	Yes	Yes
C3/SMF-S1	Yes	Yes	Yes
C3/PCE-D1	Yes	Yes	Yes
C4/LS-C1	**No**	**Yes**	**No**
C4/SNF-S1	Yes	Yes	Yes
C4/SNF-D2	Yes	Yes	Yes
C4/SNF-C2	**No**	**No**	**No**
C4/SMF-S1	Yes	Yes	Yes
C4/PCE-D1	Yes	Yes	Yes

*****Could not be determined

The compatibility of different combinations are studied as per the criteria given in step 1. Accordingly, C2/LS-C1 and C4/LS-C1 seem to be incompatible at 0-minutes as the saturation dosages are more than the recommended limit. C4/SNF-C2 is also incompatible at 0-minutes as per both criteria; the saturation dosage is above the recommended limit and the setting time is more than 16 hours. The incompatible combinations are marked with bold letters.

The test results at 60-minutes give more incompatible combinations due to the significant loss of fluidity in some combinations (see Figure 6.1(a-d)). Accordingly, C1/SMF-C1, C3/LS-C1 become incompatible as their saturation dosages are above the manufacturer's recommended limit whereas the absence of a well-defined saturation dosage makes C2/LS-C1, C4/LS-C1 and C4/SMF-S1 incompatible. The SNF-C2 is also incompatible due to the same reasons as mentioned for 0-minutes.

Table 6.10 Summary of Superplasticized paste combinations at 60-minutes

Mix Compositions	Saturation dosage within the manufacturer's recommended limit at 60 min	Final Setting ≤ 16 hr	Compatible?
C1/LS-C1	Yes	Yes	Yes
C1/SNF-S1	Yes	Yes	yes
C1/SNF-D1	Yes	Yes	Yes
C1/SNF-D2	Yes	Yes	Yes
C1/SNF-C1	Yes	Yes	Yes
C1/SMF-S1	Yes	Yes	Yes
C1/SMF-C1	**No**	**Yes**	**No**
C1/PCE S1	Yes	Yes	Yes
C1/PCE-D1	Yes	Yes	Yes
C2/LS-C1	**No**	*****	**No**
C2/SNF-S1	Yes	*	Yes
C2/SNF-D2	Yes	*	Yes
C2/SMF-S1	Yes	*	Yes
C2/PCED1	Yes	*	Yes
C3/LS-C1	**No**	**Yes**	**No**
C3/SNF-S1	Yes	Yes	Yes
C3/SNF-D2	Yes	Yes	Yes
C3/SNF-C2	Yes	Yes	Yes
C3/SMF-S1	Yes	Yes	Yes
C3/PCE-D1	Yes	Yes	Yes
C4/LS-C1	**No**	**Yes**	**No**
C4/SNF-S1	Yes	Yes	Yes
C4/SNF-D2	Yes	Yes	yes
C4/SNF-C2	**No**	**No**	**No**
C4/SMF-S1	**No**	**Yes**	**No**
C4/PCE-D1	Yes	Yes	Yes

*****could not be determined

The literature gives other approaches to identify the compatible cement-superplasticizer combinations. According to Aïtcin (1998), in a cement-superplasticizer combination, if the 0 minutes Marsh cone flow time curve and 60 minutes flow time curve intersect or are close to each other, it can be considered as a compatible combination, and the saturation dosage is taken as the dosage at the point of intersection of the curves. According to Aïtcin's criterion, all the combinations studied here are compatible, except those with the superplasticizer LS-C1 with the cements C2, C3 and C4. The combinations that are incompatible according this criterion are also incompatible as per the proposed selection criteria, which is however, more stringent (by taking into consideration the setting of the paste) leading to more incompatible combinations.

Furthermore, Nkinamubanzi et al. (2000) has classified the compatibility of different cements through their chemical compositions. They suggested the use of the SO_3/C_3A ratio and alkali content for selecting compatible combinations. Figure 6.7 attempts to classify the tested cements accordingly. According to Nkinamubanzi et al. (2000), a high SO_3/C_3A ratio and high alkali content are considered as the requirements for compatibility. Consequently, the cements C1, C2 and C3 are classified as compatible and cement C4 is less compatible due to a low SO_3/C_3A ratio. Note that the SO_3 present is considered to be completely soluble, which may not be always the case. According to the proposed method (see test results in Tables 6.9 and 6.10), the cement C4 has more incompatible combinations, and therefore, can be considered as less compatible than the other cements, which is in accordance with the classification of Nkinamubanzi et al. (2000).

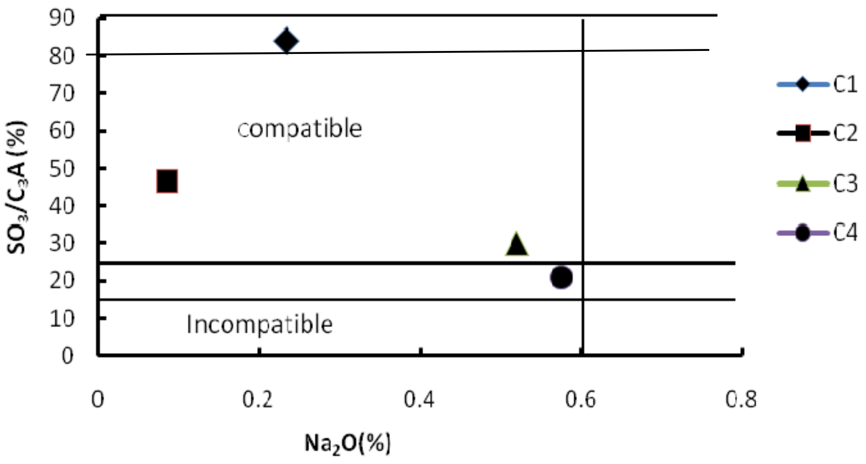


Fig. 6.7 Classification of cement based on its chemical composition
(based on Nkinamubanzi, et al., (2000)

6.7 SUMMARY

The influence of the chemical composition of cement and family of superplasticizers on the flow and setting behaviour of different pastes are analysed in the present chapter. It is confirmed that both the fresh and hardening properties vary for different combinations. In order to understand this difference in nature, the absorbance of the admixtures has been determined, as the rate and amount of adsorption of superplasticizers on cement surfaces is responsible for the effective dispersion. Also, the UV absorbance at different times helps understand the mechanisms that cause the loss of fluidity of superplasticized pastes. This study confirms that a good correlation exists between the loss of fluidity with initial adsorption. In addition to that, the λ_{max} is found to be a characteristic of a particular superplasticizer and hence UV absorbance can be used as a simple test to identify the family of superplasticizer. Finally, a simple methodology based on the flow and setting behaviour of pastes is suggested to identify the compatible cement-superplasticizer combinations and is validated with other approaches from the literature.

CHAPTER 7

FLOW BEHAVIOUR OF SUPERPLASTICIZED PASTES INCORPORATING OTHER ADMIXTURES

7.1 GENERAL

An objective procedure for determining the saturation dosage of superplasticizer in a cement paste using the Marsh cone test has been explained in Chapter 3 for understanding the flow behaviour of the paste. The experimental and analytical correlation between the Marsh cone flow times with rheological parameters has also been presented. The flow behaviour of the paste was found to relate well to the fresh state properties of normal concrete showing the relevance of conducting the tests on paste. These procedures applied for understanding the behaviour of superplasticized cement paste are extended in the present Chapter to pastes with other admixtures such as metakaolin and viscosity modifying agents.

The incorporation of mineral admixtures, viscosity modifying admixtures (VMA) and superplasticizers in the paste composition results in a balance between the cohesion and fluidity of special cement-based materials such as cement grouts, shotcrete, underwater concrete and self compacting concrete (SCC) (Khayat and Guizani, 1997; Lachemi et al., 2004, 2007). Superplasticizers generally decrease the yield stress whereas viscosity modifying admixtures tend to increase the viscosity at the same w/c ratio (Ferraris et al., 2001; Sonebi, 2006). Moreover, the interaction between different admixtures in a cementitious system sometimes results in delays in setting time and rapid slump loss, which demand a compatible combination to achieve the best rheological properties (Khayat and Yahia, 1997).

The objective of this chapter is to understand the flow behaviour of superplasticized paste with components such as mineral admixtures and VMAs. The work is of particular interest for the development of self compacting concrete (SCC) as it generally incorporates both the superplasticizer and viscosity modifying agent.

The present chapter details the procedures and results of tests performed with the Marsh cone, mini-slump and viscometer on superplasticized pastes with metakaolin or a VMA. For correlating the results from the tests on pastes, an experimental study of the fresh behaviour of SCC was done through its characteristic tests like slump flow, V-Funnel, J-Ring in addition to compression tests. Based on the results, the methodology of Gomes et al. (2001) and Gettu et al. (2004) for the mix design is extended to SCC incorporating a VMA.

7.2 MATERIALS USED IN THE STUDY

53 grade ordinary portland cement (cement C1), PCE-D1 and SNF-D2 superplasticizers, metakaolin and four types of VMAs are used in the study. The characteristics of cement and superplasticizers have already been reported in Chapter 3.

The commercial availability of metakaolin in India has increased in the last few years due to extensive kaolin sources across the country (Kumar and Kaushik, 2003). Metakaolin is a primary product formed by the calcination of kaolin clay at a temperature of 650-800°C. It belongs to the chemical family of China clay-aluminium silicate (Al_2O_3 $2SiO_2$). It contains 50-55% SiO_2 and 40-45% Al_2O_3. Its specific gravity is 2.6, bulk density is 300 kg/m^3 and specific surface is 12000m^2/kg. Additional, C-S-H is produced due to its reaction with $Ca(OH)_2$ as indicated in Equation 7.1:

$$AS_2 + 6CH + 9H \rightarrow C_4AH_{13} + 2C\text{-}S\text{-}H \qquad (7.1)$$

Four types of VMAs were used in the study with the properties given in Table 7.1. VMA 4 is diutangum whereas the others are liquids based on polysaccharides.

Table 7.1 Properties of viscosity modifying agents

Name of VMA	Density (gm/ml)	Solid content (%)	appearance
VMA 1	1.02	2	liquid
VMA 2	1.00	2	liquid
VMA 3	1.01	2	liquid
VMA 4	-	100	powder

7.3 FLOW BEHAVIOUR OF PASTES WITH METAKAOLIN

Metakaolin is said to increase the total volume of finer pores and decrease the volume of coarser pores; however, the total volume of pores is reported to be less than in pure cement paste (Khatib and Wild, 1996). Its density is lower than that of cement whereas the surface area is higher with irregular shape particles. Consequently, the flow behaviour is affected by the incorporation of metakaolin with higher loss of fluidity and more shear thickening when compared with pure cement paste (Cyr et al., 2000; Corinaldesi and Moriconi, 2003; Li and Ding, 2003).

It has also been reported that metakaolin increases the water demand and apparent viscosity of paste due to an increase in the solid fraction of paste. The superplasticizer type appears to significantly affect the workability and compressive strength of mortar and concrete incorporating metakaolin as the rate of pozzolanic reaction and hydration depends on the type of superplasticizer; Kim et al. (2003) found that SNF blends and PCE cause slump retention whereas the SNF and SMF cause slump loss. It was also reported that the PCE retards the hydration reaction and hence causes a reduction in compressive strength.

7.3.1 Effect of Metakaolin in Paste incorporating PCE Based Superplasticizer

For the pastes, cement and metakaolin were taken in the ratio of 90:10 and the water/powder ratio (w/p) was taken as 0.35. The Marsh cone, mini-slump and viscometer tests were conducted immediately after mixing (0 minutes) and after 60 minutes. The trend observed in the Marsh cone flow time with metakaolin is same as that of cement-PCE combination with a decrease in flow time with an increase in the dosage of superplasticizer. All the combinations seem to exhibit well defined saturation points. The addition of metakaolin increases the saturation superplasticizer dosage from 0.1% to 0.2% (in terms of solid content of sp/c%), as shown in Figure 7.1, which may be due to the increase in solid fraction and surface area in the paste. The loss of fluidity is also observed to be higher than in the cement-superplasticizer combination, which confirms earlier results (Li and Ding, 2003). The level of flow at the saturation dosages are, however, practically the same.

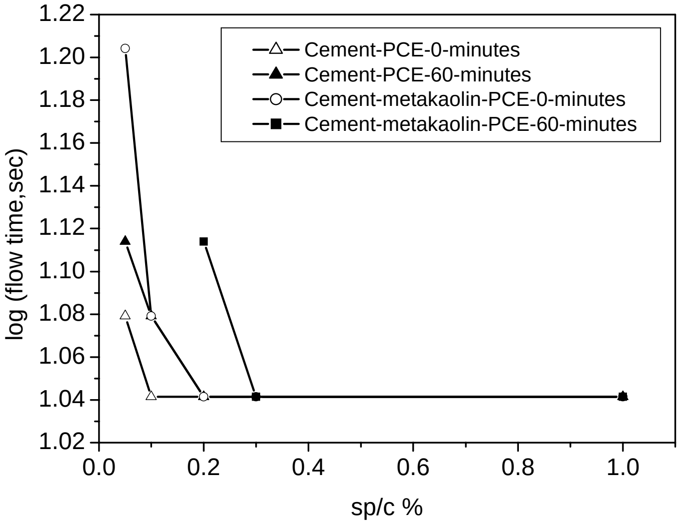


Fig. 7.1 Marsh cone flow time curves for pastes with metakaolin and PCE based superplasticizer

The mini-slump spread increases with an increase in the dosage of superplasticizer in the cement-superplasticizer-metakaolin combination, as seen in Figure 7.2. At 0 minutes, both the pastes exhibit bleeding beyond the saturation dosage, and hence the corresponding data are not plotted in the graph. The addition of metakaolin decreases the mini-slump spread, as shown in Figure 7.2.

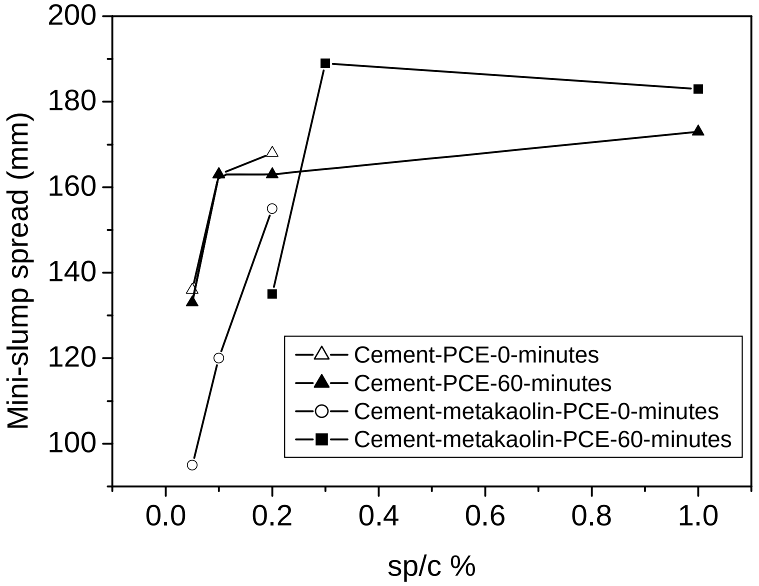


Fig. 7.2 Variation of mini-slump spread with dosage of PCE for metakaolin-PCE combination

The rheological study of the pastes showed that the addition of metakaolin results in an increase in the yield stress at low dosages and remains constant beyond the saturation dosage of superplasticizer, as seen in Figure 7.3. The plastic viscosity also increases with the addition of metakaolin, especially at low dosages of superplasticizer, as shown in Figure 7.4. With regards to both the parameters, the addition of metakaolin does not produce any significant difference in the rheological parameter beyond the saturation dosage. The observed trends are in disagreement with the reported results of Ferraris et al. (2001), who did not find any significant increase in the yield stress or viscosity due to the addition of metakaolin mix. However, the present data are in accordance with the results of Cyr and Mouret (2003). It is possible that the variations in the properties of the metakaolin lead to the differences in the conclusions drawn from the different studies.

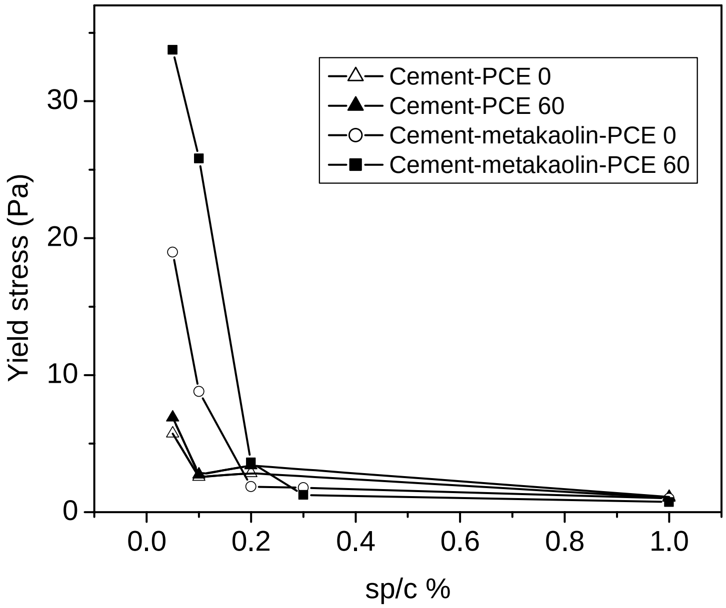


Fig. 7.3 Variation of yield stress with dosage of PCE for metakaolin-PCE combination

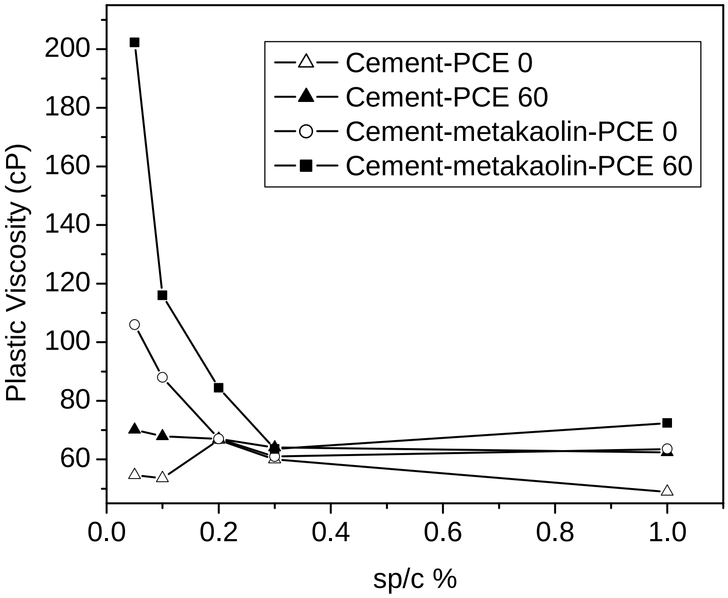


Fig. 7.4. Variation of plastic viscosity with dosage of PCE for Metakaolin-PCE combination

7.3.2 Effect of Metakaolin in Paste Incorporating SNF Based Superplasticizer

The flow curves at 0-minutes and 60-minutes for the cement-metakaolin-SNF based paste are shown in Figure 7.5. The flow curves at 0-minutes shows that the addition of metakaolin increases the saturation dosage of SNF. In spite of the retarding effect of the superplasticizer SNF-D2, there is a significant loss of fluidity within 60-minutes in the paste with metakaolin and a well defined saturation dosage cannot be obtained for the flow curve corresponding to 60-minutes. This may be either due to incompatibility between the metakaolin and SNF, as reported by Kim et al. (2003), caused by the absorption of SNF by the metakaolin. The addition of metakaolin decreases the mini slump spread at 0-minutes as well as for 60-minutes (see Figure 7.6) confirming the results of Kim et al. (2003). The viscometer test results also shows the same trend, with an increase in yield stress and plastic viscosity with an increase in the time after mixing (see Figures 7.7 and 7.8).

The comparison of test results shows that SNF causes more loss of fluidity than PCE based superplasticizer and is significantly less compatible with the metakaolin than the PCE. The results also show that a compatible cement-superplasticizer combination can give incompatibility related problems, such as loss of fluidity, when a mineral admixture is incorporated.

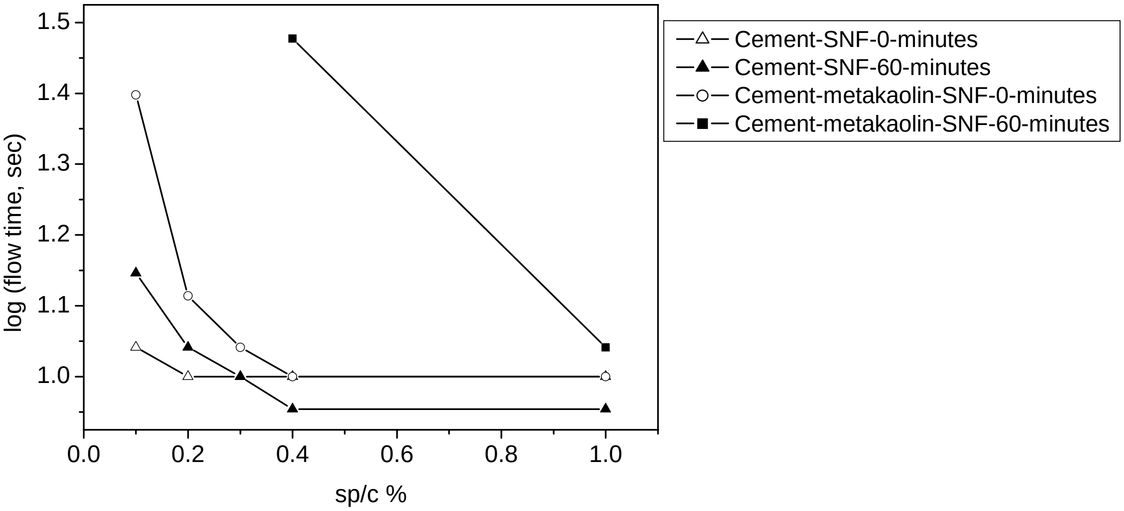


Fig. 7.5 Marsh cone flow time curves for pastes with metakaolin and SNF-D2

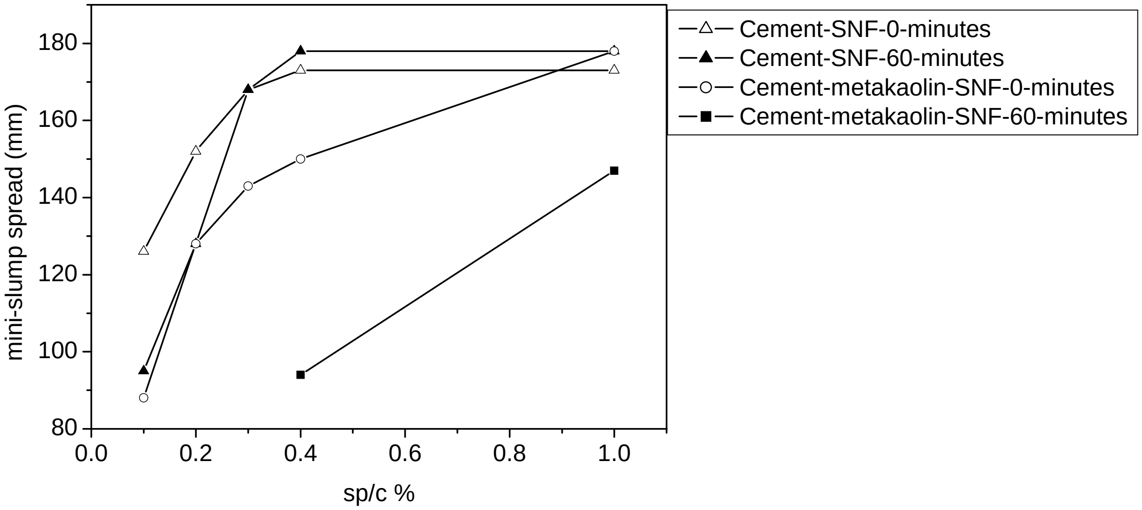


Fig. 7.6 Variation of mini-slump spread for pastes with metakaolin and SNF-D2

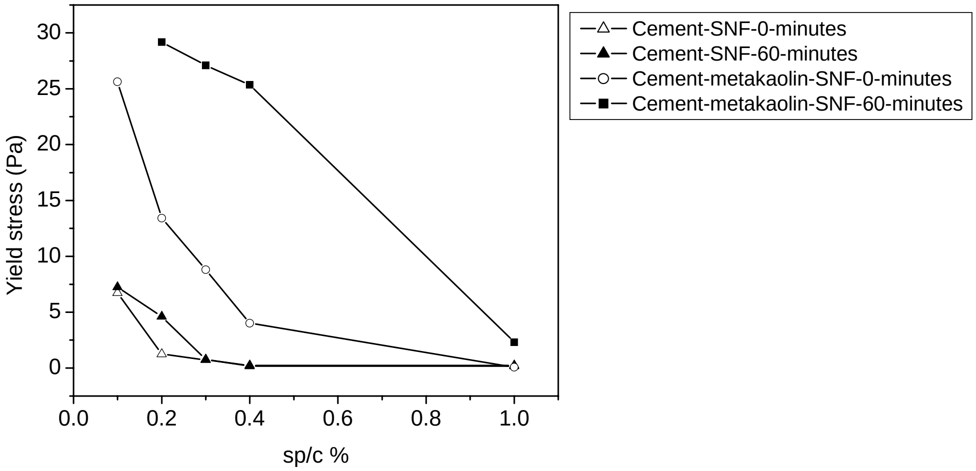


Fig. 7.7 Variation of yield stress for paste with metakaolin and SNF-D2

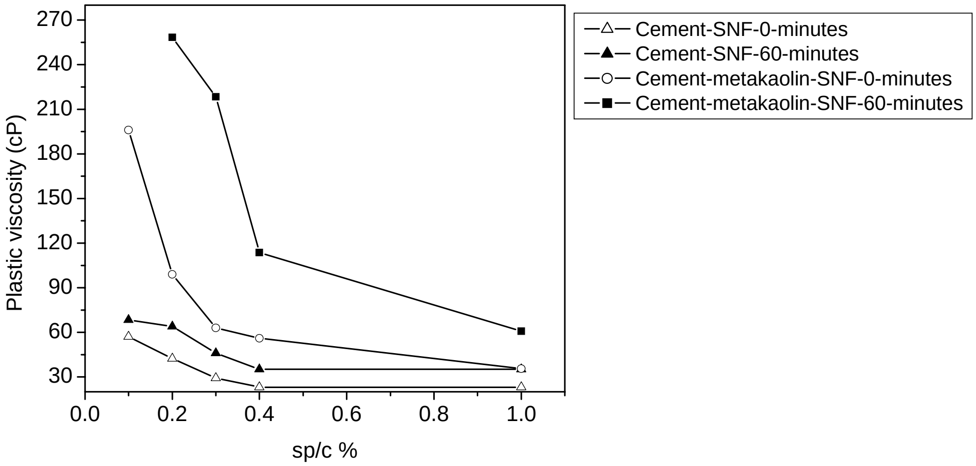


Fig. 7.8 Variation of plastic viscosity for paste with metakaolin and SNF-D2

7.4 INFLUENCE OF VMA ON THE FLOW BEHAVIOUR OF SUPERPLASTICIZED PASTE

7.4.1 Characteristics of VMA

VMAs are water soluble polymers that increase the viscosity of the paste and enhance the ability of the paste to retain its constituents in suspension (Khayat and Yahia, 1997; Lachemi et al., 2007). The main function of the VMA is to modify the rheological properties of cement paste. As mentioned earlier, the rheological behaviour of fluid cement pastes can be described by the yield stress and plastic viscosity. The VMA changes the rheology by increasing the plastic viscosity but with a small increase in yield shear stress. On the other hand, superplasticizers tend to decrease the yield stress. In conjunction, the superplasticizer and VMA can be used to optimize the yield shear stress. The test methods used are those explained earlier were used here to understand the flow behaviour of paste incorporating VMA.

VMAs are either cellulose or polysaccharide based, and they are classified as natural, semi-synthetic or synthetic polymers. Natural polymers include starches, guar gum, locust bean gum, alginates, agar, gum Arabic, welan gum, xanthan gum, rhamsan gum, and gellan gum, as well as plant protein. Semi-synthetic polymers include decomposed starch and its derivatives, cellulose-ether derivatives such as hydroxypropyl methyl cellulose (HPMC), hydroxyethyl cellulose (HEC) and carboxy methyl cellulose (CMC), as well as electrolytes such as sodium alginate and propylene glycol alginate. Synthetic polymers consist of polymers based on ethylene such as polyethylene oxide, polyacrylamide, polyacrylate and those based on vinyl such as polyvinyl alcohol (Khayat and Yahia, 1998). According to their physical action, VMAs are classified into five categories (Rixom and Mailvaganam, 1999):

Class A: Water-soluble synthetic and natural organic polymers that increase the viscosity of the mixing water. These types of materials include cellulose ethers, polyethylene oxides, polyacrylamide, polyvinyl alcohol etc.

Class B: Organic water-soluble flocculants that become adsorbed on cement grains and increase the viscosity due to enhanced interparticle attraction between cement grains. It includes styrene copolymers with carboxyl groups, synthetic polyelectrolytes and natural gums.

Class C: Emulsions of different organic materials that enhance interparticle attraction and supply additional superfine particles in the cement paste. The materials belonging to Class C are acrylic emulsions and aqueous clay dispersions.

Class D: Water-soluble inorganic materials having high surface area that increase the water retaining capacity of the paste such as bentonites, silica fume, and milled asbestos.

Class E: Inorganic materials having high surface area which increase the content of fine particles in paste and hence the thixotropy. They include fly ash, hydrated lime, kaolin, various rock dusts, and diatomaceous earth, etc.

7.4.2 Experimental Details

The methodology used for the mix design of SCC in the present study is an extension of an approach proposed by Toralles-Carbonari et al. (1996) for high strength silica fume concrete and later modified by Gomes et al. (2001) and Gettu et al. (2004) for SCC. Within this approach, concrete is considered as a two phase material consisting of a paste that provides fluidity and cohesion, and an aggregate skeleton that provides the mechanical integrity. The flow behaviour of paste and concrete is studied in the present work by varying the type and dosage of superplasticizer and VMA, while keeping the other parameters such as temperature and cement type constant.

7.4.2.1 Study of the Interaction between Superplasticizer and VMA

The mixing method for the preparation of paste is same as that used in the preparation of superplasticized cement paste, except that the VMA is added after three minutes and it is further mixed for 2 minutes. The flow behaviour of the paste was determined using Marsh cone, mini-slump and viscometer. Preliminary tests were conducted with three different types of VMAs (VMA 1, VMA 2 and VMA 3) and a PCE based superplasticizer at two w/c ratios (w/c = 0.5 and w/c = 0.35) to understand the superplasticizer-VMA interaction. The saturation dosage of the superplasticizer was determined as 0.2% and trials were conducted with a low dosage of 0.3% of different VMAs. This study identified the VMA leading to the highest Marsh cone flow time and the least mini-slump spread as VMA 1; see Figures 7.9 and 7.10 (VMA 0 denotes the mix without VMA). This was considered as the most effective in terms of achieving the cohesion compared to the other VMAs and hence it is used for further studies. Also, it is observed that the effectiveness of the VMA increases with a decrease in w/c as shown in Figures 7.9 and 7.10. This may be because, the molecules in adjacent polymer chains can develop attractive forces at low w/c, further blocking the movement of water, causing gel formation and a consequent increase in viscosity (Khayat and Guizani, 1997). The plastic viscosity also shows the same trend as the Marsh cone flow time and mini-slump spread and is given in Figure 7.11.

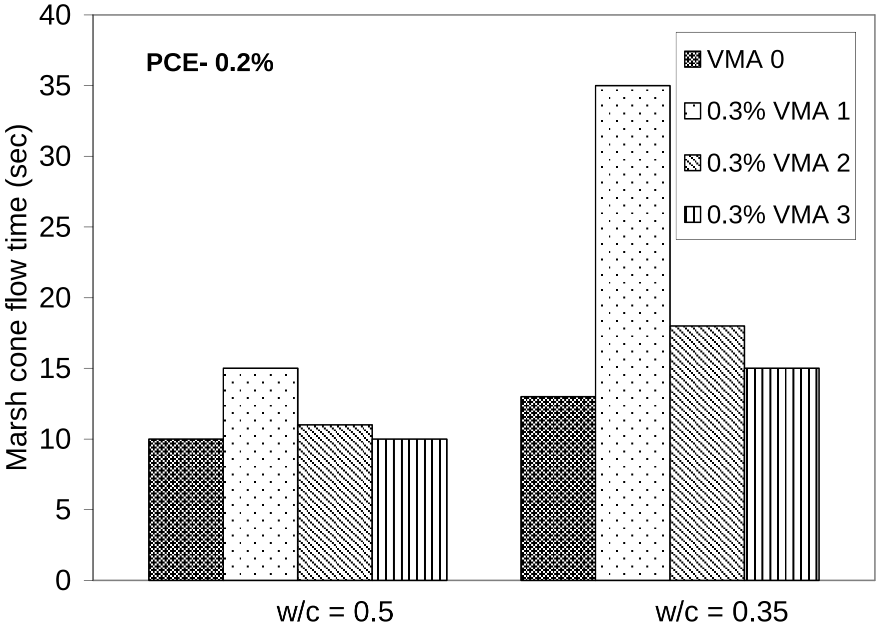


Fig. 7.9 Marsh cone flow time for different viscosity modifying agents

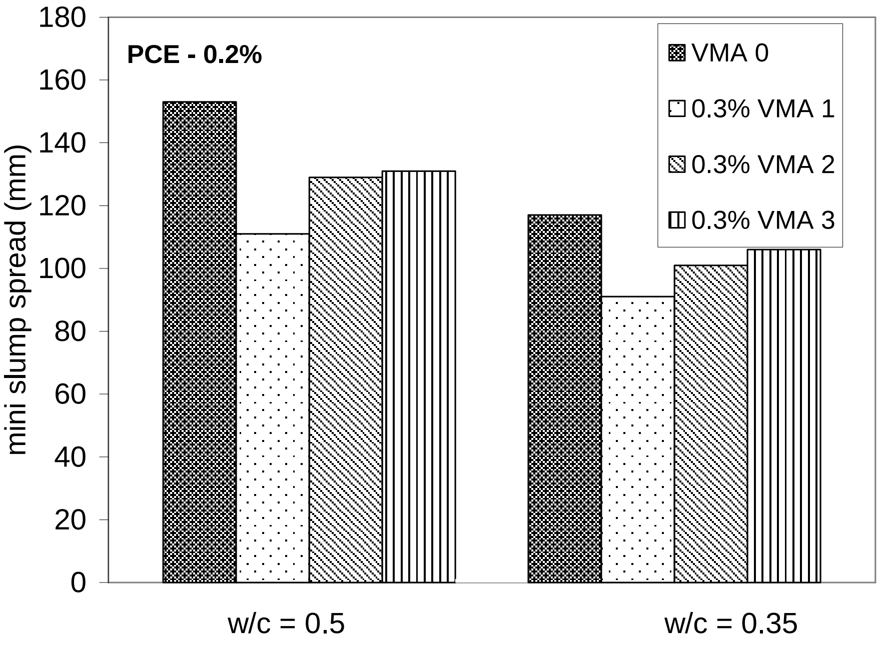


Fig. 7.10 Mini slump spread for different viscosity modifying agents

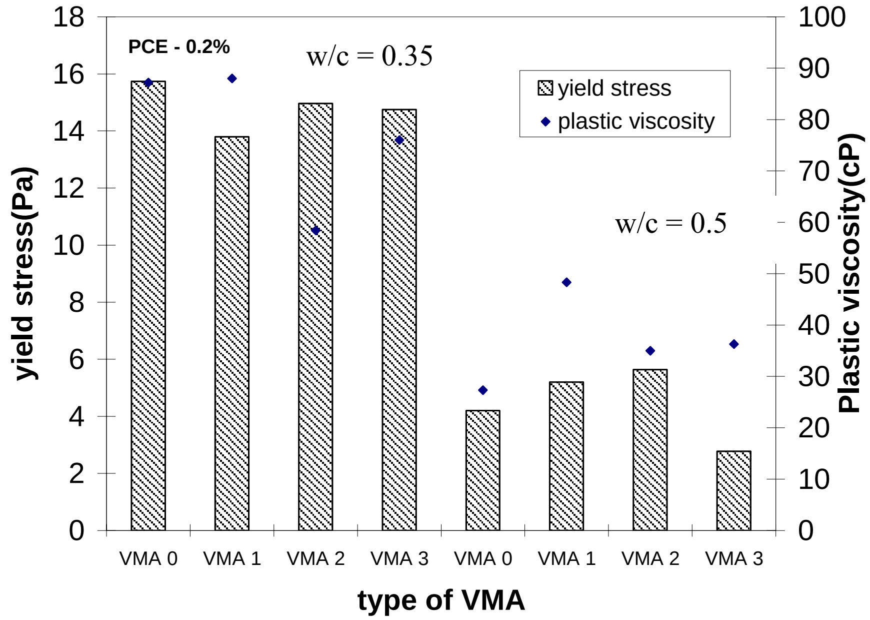


Fig. 7.11 Values of yield stress and plastic viscosity for different viscosity modifying agents

With the w/c ratio set at 0.35, Marsh cone flow time curves were determined for low and high dosages of VMA 1 with different dosages of superplasticizer (PCE-D1) The test results are given in Figure 7.12; where it can be observed that Marsh cone flow time increases with an increase in the dosage of the VMA. For comparison, results are also reported for a Welan gum based VMA, namely VMA 4, at the dosages that are normally used. It is seen that VMA 4 leads to higher flow times than VMA 1 at both dosages.

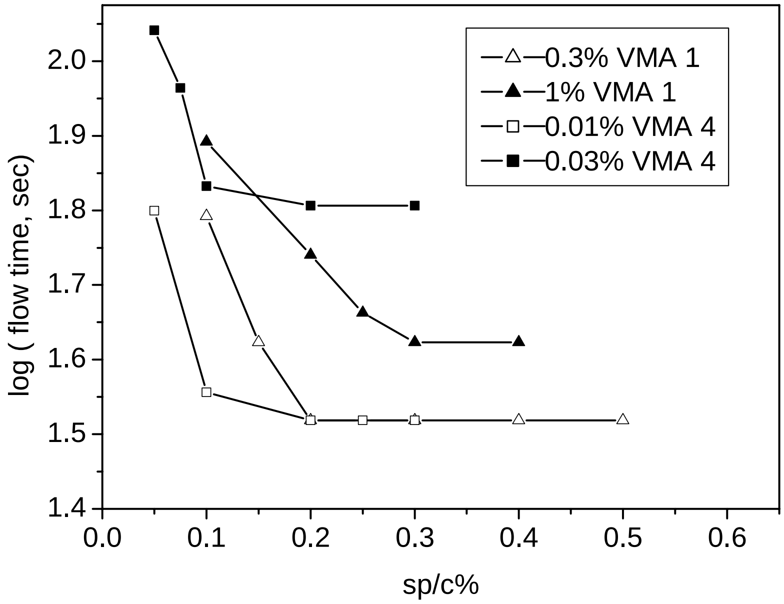


Figure 7.12 Determination of saturation dosage of superplasticizer at different dosages of VMA

The mini-slump spread, the spread time to reach a diameter of 115 mm (t_{115}) and rheological parameters were determined for different dosages of VMA with the corresponding saturation dosages of superplasticizers from paste tests. The results are summarized in Table 7.2. Gettu et al. (2004) recommend a value of about 2 seconds for t_{115} to obtain a paste with adequate cohesion for SCC, which is obtained in all the present cases. However, their requirement of a minimum spread of about 170 mm is not met, except in the case of VMA 4 at a dosage of 0.01%.

Table 7.2 Flow characteristics of pastes with different types and dosages of VMA

Saturation dosage of SP (sp/c %)	Type and dosage of VMA (%)	Flow time (sec)	Mini-slump spread (mm)	t_{115} (sec)	Yield stress (Pa)	Plastic viscosity (cP)
0.2	VMA 1 - 0.3	34	133	2	4	126
0.3	VMA 1 - 1.0	66	112	3	3	130
0.2	VMA 4 - 0.01	49	168	2	0	282
0.2	VMA 4 - 0.03	68	140	2	*	*

* values could not be measured

7.4.2.2 Effect of Time on the Flow Behaviour of Paste Incorporating Superplasticizer and VMA

The effect of VMA to increase as well as to maintain the viscosity depends on the type of superplasticizer and type of VMA (Khayat and Yahia, 1997). In order to understand the efficiency of VMA to maintain the cohesion for longer period, flow tests were conducted at 0, 30, 60 and 90 minutes with PCE-D1 based superplasticizer and VMA 1 and VMA 4 at a w/c of 0.35. The saturation dosage of superplasticizer for different combinations were determined as explained in Section 7.4.2.1.

The rheological parameters were also investigated at low and high dosages of VMA. The Marsh cone test results of different combinations are shown in Figure 7.13 and the summary of flow test results are given in Table 7.3. The test results at different ages show that only in the paste with PCE-D1 and VMA 4, the Marsh cone flow time increases with time. It is observed that in other combinations, instead of increasing, the Marsh cone flow time decreases with time. The mini-slump test result also supports the Marsh cone results; the mini-slump spread decreases with time in PCE-D1-VMA 4 combination. The t_{115} value also increases with time in the same combination. This shows that even though VMA 1 is effective in giving cohesion and stability to the paste initially, it is not effective in maintaining the cohesion and fluidity even for a period of 60-minutes. This is because the yield stress of paste in this combination is very low and the mix loses its cohesiveness as the plastic viscosity decreases with time.

Here, it is seen that VMA 4 is more effective in increasing, as well as maintaining the viscosity of the paste than VMA 1. This may be due to the difference in the chemical structure of the two VMAs.

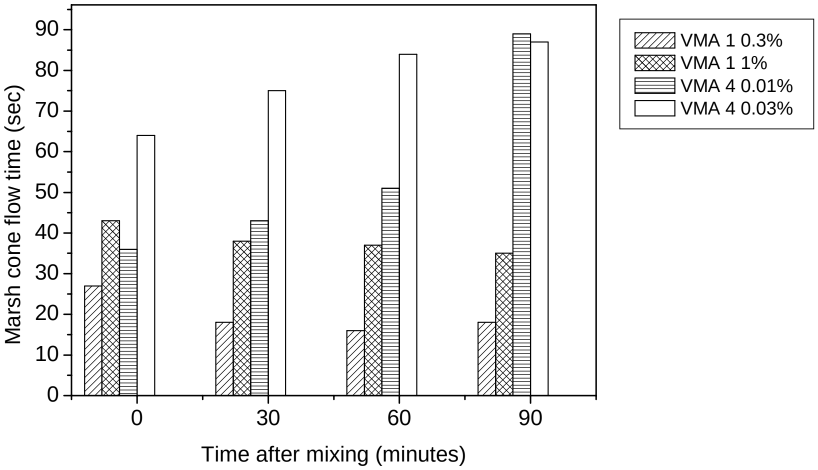


Fig. 7.13 Effect of time on Marsh cone flow curves of SP-VMA mix

Table 7.3 Influence of time on SP-VMA mix

Type an dosage o SP (sp/c%)	Type and dosage of VMA (%)	Time afte mixing (min)	Flow time (sec)	Mini-slump spread (mm)	t_{115} (sec)	Yield stress (Pa)	Plastic viscosity (cP)
PCE- D1 0.2%	VMA 1 0.3%	0	27	115	2	4.5	121
		30	18	125	1	3.8	82.4
		60	16	122	1	3.6	85.7
		90	18	140	1	3.3	84.4
PCE- D1 0.3%	VMA 1 1%	0	43	147	3	0	125
		30	38	155	2	0	107
		60	37	145	1.5	0	93
		90	35	154	1	0	95
PCE-D1 0.2%	VMA 4 0.01%	0	36	148	1.5	1.6	235
		30	43	149	2	2.9	263
		60	51	135	3	5.4	260
		90	89	109	6	8.6	285
PCE-D1 0.2%	VMA 4 0.03%	0	64	138	2	*	*
		30	75	128	3	*	*
		60	84	123	4	*	*
		90	87	115	5	*	*

* data could not be determined

7.5 COMPARISON OF THE FLOW BEHAVIOUR OF PASTE AND SELF COMPACTING CONCRETE

7.5.1 Mix design and testing of SCC

The procedure for the determination of the saturation dosage of superplasticizer in the paste phase with VMA has been explained in Section 7.4, with the intention of obtaining a paste with good cohesion and fluidity, which are essential for the flowability and resistance to segregation of highly workable concretes. Since adequate flow behaviour of paste is fundamental for achieving concrete with adequate fluidity and viscosity, tests have been performed on SCC to validate the paste test results, as done for normal concrete in Chapter 4. The mix proportioning of SCC is performed by separately determining the saturation dosage of superplasticizer for prescribed dosages of VMA in the paste phase, optimizing the aggregate proportion for minimum void content, and then the paste content of the concrete to get the final composition, following the method of Gomes et al. (2001).

As the first step in the mix design of SCC, the paste phase is optimized for high fluidity and adequate cohesion. In the method of Gomes et al. (2001), a paste with the saturation dosage of superplasticizer, as determined from the Marsh cone test, and meeting the criteria of mini-slump spread of about 170 mm and a t_{115} of about 2 seconds (Gettu et al., 2004) is considered to be appropriate for SCC. The pastes studied in the previous section with the superplasticizer and VMA dosages given in Table 7.2, and with a w/c of 0.35, satisfied the above-mentioned criteria for pastes, except for the requirement of a spread of about 170 mm that is met only in the case of 0.01% dosage of VMA 4. Nevertheless, SCC mixes were developed for all the four pastes for further evaluation.

For the definition of the aggregate skeleton, the maximum aggregate size was limited to 20 mm in order to have high fluidity without segregation. The optimum aggregate combination is selected by considering the packing density and lowest void content with the assumption that minimum void content leads to the minimum paste volume, porosity and shrinkage. However, concrete requires more paste content than the minimum void content to ensure cohesion and fluidity. The aggregate phase is optimized here by measuring the dry uncompacted density of aggregate mixes and choosing the mix with least void content (Gomes et al., 2001). The method is same as that given in ASTM C29/C29M (2007), except that the uncompacted weight is taken, which is more suitable for SCC.

In the present study, the sand, and coarse aggregates with maximum grain sizes of 20 mm and 10 mm were dry mixed manually in a tray and placed in a 15 litre container without any compaction. The proportions of the 5-10 mm : 10-20 mm fractions were fixed as 3:2. The density or unit weight was measured to determine the void content, as shown in Figure 7.14. It was observed that the sand content that gave the minimum void content was 45 %, with a void content of 28%.

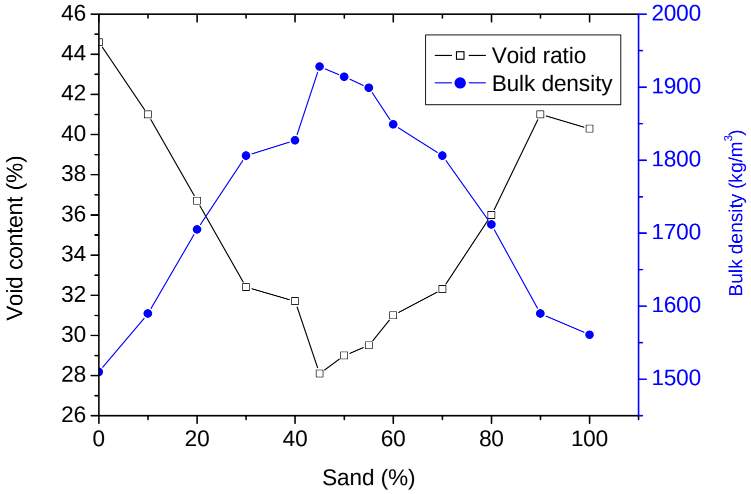


Fig. 7.14 Determination of aggregate proportions for concrete

The SCC has to satisfy certain requirements in the fresh and hardened state .The filling ability and stability of SCC in the fresh state can be defined by four key characteristics, which can be determined by the following test methods recommended by EFNARC Guide lines (2005), Italian UNI standards and ASTM C1621 (2006) code.

Flowability	Slump flow test
Viscosity and segregation resistance	T_{500} or V-Funnel test
Passing ability	J-Ring test

The following are the acceptance criteria of SCC that were prescribed based on the above test methods.

Table 7.4 Acceptance criteria for SCC

Test	values
Slump flow	550-700 mm
Slump flow spread time (T_{500})	2-5 sec
V-funnel flow time	10 ± 3 sec
Difference in V-funnel flow time between measurements made immediately and after 5 minutes	≤ 3 sec
Difference between J ring Flow and slump flow	< 50 mm
28 days compressive strength	>50 MPa

In the present study, the slump flow, V-funnel and J-ring tests have been conducted for characterizing the self compacting concrete (EFNARC Guidelines for SCC, 2005). In addition to that the compressive strength of concrete has been determined at 3 days, 7 days and 28 days.

Slump flow test is a simple method to evaluate the filling ability of SCC under its own weight. The test method is shown in Figure 7.15. The slump cone is filled with concrete without compaction and is lifted to allow the concrete to flow over a plain surface. The time for 50cm spread (t_{50}) is measured along with the final spread as the average of two perpendicular diameters. The concrete is visually examined for the segregation and bleeding.

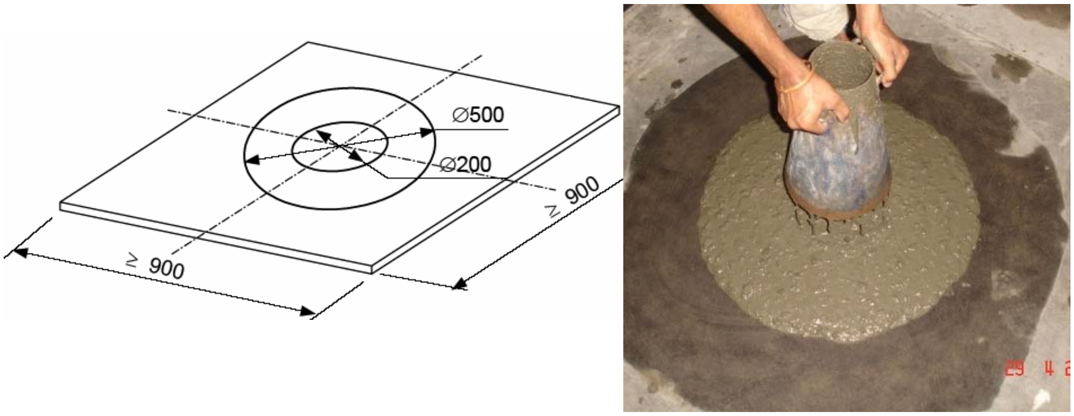
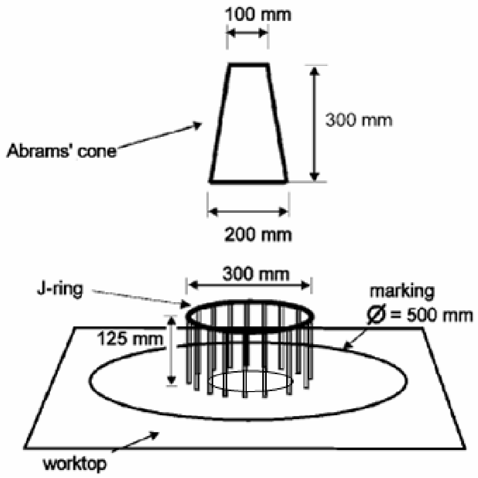


Fig. 7.15 (a) Slump cone measurements (b) Slump Cone test

A combination of slump flow with a ring denoted as J-Ring has been used to study the blockage due to reinforcement (see Figure 7.16). As in the case of slump flow test, the slump cone kept inside the J-Ring is filled with concrete. The concrete flows through the gaps as the cone is lifted. The final spread is measured in two perpendicular directions which gives an idea about the passing ability of concrete.

(a)



(b)

Fig. 7.16 (a) J-Ring measurement (b) J-Ring test

The V-funnel test method consists of measuring the time taken for a certain volume (approximately 10 litres) of concrete to flow through a funnel (see Figure 7.17). The funnel is again filled with the same concrete and waited for 5 minutes. The outlet is opened after 5 minutes and the time taken for it to flow is noted. The difference between the initial and final time should be less than 5 seconds so as to satisfy the characteristic of SCC. Thus the test gives a good indication of viscosity of the paste as well as an indication of segregation.

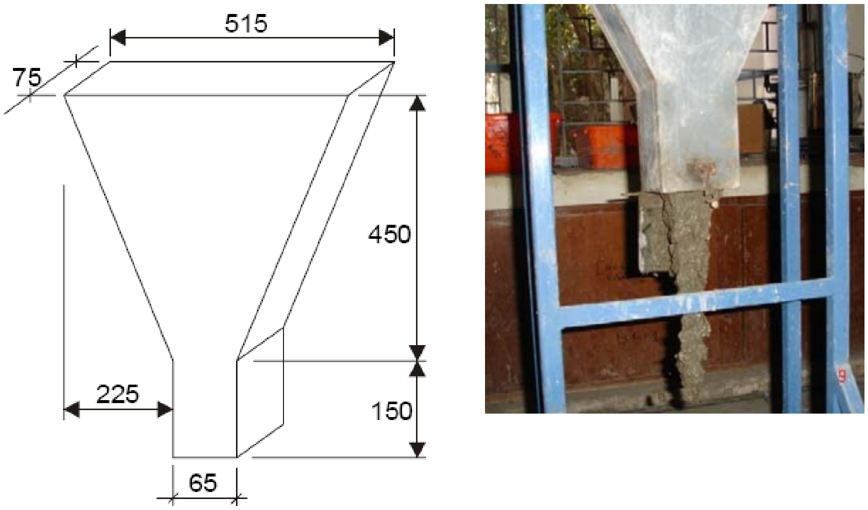


Fig. 7.17 V-Funnel test

The trial mixes showed that adequate paste content is needed for achieving a satisfactory SCC. Here, the paste volume was set as 38%, which is about 10% more than the void content determined in the aggregate compaction tests. The mix proportions used for the SCC tests are given in Table 7.5; the paste compositions are the same those characterized in Section 7.4 except that the superplasticizer dosage has been varied to evaluate the influence of the same. The aggregates used have been described already in Chapter 5.

Table 7.5 Proportion of materials used in the SCC trials

Cement Kg/m^3	Water Kg/m^3	Fine aggregate Kg/m^3	Coarse aggregate		Superplasticizer – PCE-D1 (sp/c %)	VMA (%)
			10 mm Kg/m^3	20 mm Kg/m^3		
550	193	800	494	332	0.1,0.2,0.25, 0.3	0.3% VMA 1
					0.25, 0.3, 0.35, 0.4	1% VMA 1
					0.1,0.2,0.25, 0.3	0.01% VMA 4
					0.2, 0.25, 0.3, 0.4	0.03% VMA 4

SCC was prepared with different dosages of superplasticizers for the different SP-VMA combinations, and with low and high dosages of VMA in each combination. The mixing procedure is same as that of normal concrete except that the total mixing time is 7 minutes in which VMA was added after 4 minutes. The slump flow, V-funnel and J-ring tests are used for studying the fresh state properties. In addition, 3, 7 and 28-day compressive strength were also determined.

The results are given in Table 7.6, with the mixes satisfying the acceptance criteria of SCC denoted in bold letters. It is observed that in all the combinations, a dosage equal to or higher than the saturation dosage is needed for obtaining an adequate slump flow. Also, other acceptance criteria are not satisfied if the dosage is lower than the saturation superplasticizer dosage. The superplasticizer dosage slightly higher than the saturation dosage results in t_{50} value less than one second, showing that the mix is not viscous enough for a stable concrete. Also the passing ability of concrete is not improved with the extra superplasticizer. An overdosage of the PCE based superplasticizer results in a reduced slump flow in some combinations as reported in the paste study. This is attributed to the shear thickening and immediate stiffening of the paste.

Table 7.6 Test results of SCC with various SP-VMA combinations

Combi-nation	sp/c (%)	Saturation dosage of sp/c from paste(%)	Slump Flow (mm)	T_{50} (Sec)	V-Funnel Time$_0$ (Sec)	V-Funnel Time$_5$ (Sec)	J ring spread (mm)	Compressive strength (MPa)		
								3 days	7 day	28 days
VMA 1 0.3%	0.1	0.2	290	*	*	*	*	33	38	43
	0.2		**665**	**2.1**	**9**	**9.1**	**590**	**36**	**47**	**56**
	0.25		675	1	4.3	5.2	610	36	39	49
	0.3		715	<1	4.81	5.93	710	42	39	54
VMA 1 1%	0.25	0.3	460	*	6.5	9.3	450	36	44	49
	0.3		475	*	7.5	11	455	39	44	56
	0.35		**580**	**2**	**5.1**	**5.6**	**575**	**38**	**43**	**59**
	0.4		565	1.41	4.9	5.7	555	37	43	52
VMA 4 0.01%	0.1	0.2	*	*	23.7	*	*	27	37	47
	0.2		**600**	**3.2**	**7.1**	**9**	**570**	**38**	**44**	**52**
	0.25		680	1.5	7	9.3	668	37	42	52
	0.3		775	<1	6	6.2	650	39	44	53
VMA 4 0.03%	0.2	0.2	545	2	12	14.3	460	39	48	54
	0.25		**645**	**2.2**	**15.4**	**15.6**	**605**	**40**	**50**	**58**
	0.3		713	1.5	13	13.2	630	40	48	59
	0.4		663	2.1	12	14	663	40	49	60

The best performance for each combination is observed at or slightly higher than the saturation dosage of superplasticizer obtained from the paste studies; an increase in dosage of 0.05% was required for the PCE at higher dosage of VMAs. The only combination that satisfies all the criteria is with 0.01% of VMA 4, which was also the paste that came closest to satisfying the criteria of Gettu et al. (2004). The compressive strength results show that the strengths achieved are satisfactory in all the mixes at the corresponding saturation dosages. The study shows that paste test results can be used as guidelines for selecting the best combination of SP and VMA with appropriate dosages for developing SCC.

7.6 SUMMARY

- The flow behaviour of paste composed of cement, superplasticizer, mineral admixture and VMA was investigated using the Marsh cone, mini-slump and viscometer tests. It is seen that Marsh cone test along with mini-slump spread is required to understand the complete flow behaviour of the paste with these compositions.
- The addition of mineral admixtures and VMA generally increases the flow time with the corresponding change in rheological properties (i.e., the yield stress and plastic viscosity increase).
- The study confirms that the interaction between other admixtures and superplasticizer depends on the type and dosage of admixture and superplasticizer, which in turn affects the fluidity and slump retention. Generally, the paste with the PCE has good initial fluidity and maintains the fluidity better than the paste with the SNF in all the tested compositions with the mineral admixture. Among the different SP-VMA combinations studied, it is seen that the PCE-VMA 4 combination is able to maintain the cohesion over time unlike the other combinations. Consequently, it is emphasized that the compatibility of the SP-VMA combination should be studied prior to use in concrete since it can affect the time dependent behaviour of the fresh concrete and result in loss of cohesion with time, in as early as 30-minutes. The slump

flow values gradually decrease and the viscosity increases as time passes, in most of the cases.

- A mix design procedure for developing SCC with VMA has been presented based on the flow tests of pastes. The study shows that the type and dosage of superplasticizer and VMA together govern the viscosity of SCC. The saturation dosage of superplasticizer obtained from paste studies were found to give good results in SCC. Consequently, it can be confirmed that the optimization of superplasticized cement paste can be used as a guideline in the preliminary selection of chemical admixtures for SCC.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

8.1 GENERAL CONCLUSIONS

Overall, the study was able to improve the understanding of the mechanisms of cement–superplasticizer interaction and their influence on concrete performance. Moreover, the effectiveness of the Marsh cone test in characterising the fluidity of cement paste and the factors to be considered while establishing the correlation between flow behaviour of paste and concrete were brought out. The salient conclusions that correspond to the fulfillment of the principal objectives of this work are given below.

- The preparation of superplasticized cement paste with four mixing methods and the comparison of the saturation dosages obtained from these mixing methods with “ball milling” to simulate the mixing of concrete, demonstrate the influence of mixing on the flow behaviour of the paste. The dependence of the fluidity of the paste and the saturation dosage of the superplasticizer on the intensity of mixing suggests that a paste prepared using Hobart with B-flat beater is representative of the paste phase of concrete.

- The establishing of a correlation between the empirical methods with the rheological parameters shows that the same trends are obtained in the Marsh cone flow time, the yield stress and plastic viscosity when there is an increase in the dosage of the superplasticizer. The prediction of Marsh cone flow time using rheological parameters further confirms the correlation.

- The correlation between the fluidity and setting of the fresh paste and that of the mortar and concrete through standard tests shows that the trends are similar in all cases. The comparison of the flow behaviour at 60-minutes shows that the aggregates increase the loss of fluidity. Further, the presence of fines in the coarse aggregate increases the superplasticizer demand for adequate workability. However, it is confirmed that the optimization of the paste phase is a preliminary step in the mix design of concrete and the appropriate type and dosage of the superplasticizer can be selected on the basis of tests on pastes.

- The use of multiple characterization techniques instead of a single method is an effective approach for the analysis of the effect of superplasticizers on the hydration processes as well as on the microstructural development. The complementary use of XRD, SEM, DTA/TG/DTG and Si NMR has given an insight into the properties of hardened cement paste. The retardation of the setting of the superplasticized paste is attributed to the delay in the formation of ettringite, as well as with the reduction in the silicate polymerization in the presence of superplasticizers. The delay in hydration is also reflected by the presence of more unhydrated particles in the micrographs of the superplasticized pastes.

- The major characteristics of cement and superplasticizer affecting the cement-superplasticizer interaction have been identified. The mechanisms of action of the superplasticizer affect its effectiveness and consequently its compatibility with cement. The major characteristics of the cement affecting the compatibility are identified as SO_3/C_3A ratio, alkali content and fineness.

Finally, a methodology, based on the test results, is suggested as a guideline for the selection of an appropriate cement-superplasticizer combination.

8.2 SPECIFIC CONCLUSIONS

The specific conclusions derived from the experimental and analytical investigations on cement-superplasticizer interaction are classified under the following topics: (i) selection of a suitable mixing method for the preparation of paste, (ii) selection of type and dosage of superplasticizer based on Marsh cone test, (iii) rheological characterization of superplasticized paste using viscometer and rheometer, (iv) establishing experimental and analytical correlation between Marsh cone test with rheological parameters, (v) validation of paste test results with normal concrete and self compacting concrete, and (vi) influence of superplasticizers on hardening and hardened state properties of concrete.

A number of tests on paste have been performed using the Marsh cone and Viscometer to confirm the effectiveness of simple test methods in bringing out the influence of superplasticizers on the flow behaviour of paste. The rheological parameters like yield stress and plastic viscosity provided ample information about the flow behaviour of paste immediately after mixing as well as at 60-minutes. The complementary use of multiple techniques to understand the effect of superplasticizers on hardened properties validates the test results even with a few number of samples.

8.2.1 Influence of Mixing Method on the Flow Behaviour of Paste

- The type of mixing affects the fluidity as well as the saturation dosage of superplasticizer. Hence, the selection of a proper mixing method for the preparation of paste is required while correlating the superplasticized paste flow behaviour with that of concrete.

- The study helps to classify the different mixing methods as less intensive, intensive, and more intensive; less intensive mixing like hand mixing leads to higher saturation dosage and low fluidity, intensive mixing using Hobart with B-flat beater, reduce the superplasticizer demand in terms of saturation dosage, more intensive mixing like blender mixing even though leads to highest fluidity, and gives higher saturation dosage than the intensive mixing.

- The study confirmed that the paste prepared with the Hobart mixer with B-flat beater simulates the paste phase of concrete. This clarifies the conflicting views in the literature regarding the preparation of paste with blender and Hobart mixer, for establishing a correlation between paste and concrete behaviour.

8.2.2 Influence of Superplasticizers on the Flow Behaviour of Paste

- A detailed study of the influence of type and dosage of superplasticizers on the flow properties of different compositions along with the determination of the saturation dosage of superplasticizer has been conducted. The Marsh cone test, a simple but effective method, has been used for measuring the fluidity. The results of this test are found to have trends comparable to the rheological parameters (i.e., yield stress and plastic viscosity) obtained from viscometric tests.

- Even though the mini-slump test is also used to understand the flow behaviour, the study showed that, in pastes with high fluidity, it is not useful for identifying the influence of superplasticizers effectively.

- The saturation dosages of a polycarboxylate based superplasticizer with the tested cements are confirmed to be less than lignosulphonates, melamines and naphthalenes. However, the loss of slump in concrete with a polycarboxylate based superplasticizer is more than in concrete with a naphthalene based superplasticizer.

- The influence of the saturation dosage of superplasticizer on the loss of fluidity, and overdosage on settling and bleeding throws light on the selection of appropriate dosage of superplasticizer in any combination. The study on loss of fluidity of paste shows that if the fluidity at a later stage is more critical to the application than the immediate fluidity, then the saturation dosage corresponding to 60-minutes or any other critical time is required for maintaining the fluidity for that duration.

- The tests using a rheometer with parallel plate attachment showed that the nature of the superplasticized paste changes from viscoelastic fluid-like behaviour to linearly viscous flow with an increase in the dosage of the superplasticizer.

- The addition of mineral admixtures and VMA makes the paste more cohesive, and increases the yield stress and viscosity as their dosages increase. Therefore, the saturation dosage of the studied superplasticizers were all observed to increase with the addition of the admixtures.

8.2.3 Comparison between Marsh Cone Flow time and Rheological Parameters

- By applying the Bingham and Herschel Bulkley models to the flow behaviour of superplasticized paste, it is seen that an increase in the dosage of the superplasticizer leads to a significant decrease in the yield stress and plastic viscosity up to saturation dosage, after which they remain practically constant.

- The prediction of Marsh cone flow time using rheological models shows that the Marsh cone test results have a fundamental basis. Therefore, it is justified that it is suitable for evaluating the relative fluidity of superplasticized paste.

8.2.4 Effect of Type and Dosage of superplasticizer on the Retardation of Setting

- The Vicat penetration test results confirmed that the superplasticizer retards the setting of cement paste due to its effect on hydration. The present study with saturation dosage of superplasticizer showed that amount of retardation mainly depends on the type of superplasticizer. The PCE and LS based superplasticizers retard more than other families.

- Electrical conductivity measurements on the cement paste have been used to characterize the setting behaviour of cement paste. It has been observed that the superplasticizer leads to retardation of the setting process, which is mainly manifested as an increase in the duration of the dormant stage; the superplasticizer that gives the highest initial setting time leads to the longest dormant period.

- Even though the superplasticizer retards the initial setting, the duration between the initial and final setting is less than in pure cement paste and is comparable for different superplasticizers. This shows that superplasticizer does not prolong the setting process once it is initiated.

8.2.5 Correlation between Paste, Mortar and Concrete

- It is found that the Marsh cone test is a satisfactory tool for comparing the flow behaviour of different pastes and their components, and for defining the saturation dosage of the superplasticizer. The saturation dosage of superplasticizer immediately after mixing and after 60-minutes is observed to be generally different. Hence, the saturation dosage corresponding to 60-minutes flow time curves is more suitable to select a superplasticizer for maintaining the fluidity for more than one hour.

- The mortar flow tests show that the incorporation of sand does not increase the saturation dosage significantly in the context of the present study. However, the loss of fluidity of mortar is higher than that of paste at low dosages and has to be considered while comparing the mortar behaviour to that of paste phase.

- Flow tests on normal concrete and self compacting concrete show that a slight increase in the saturation dosage of superplasticizer is required for adequate workability in all combinations. This is attributed to the excess of fines in the coarse aggregate used here.

- The comparison of the setting of paste and concrete showed that even though the setting times are not directly related, the trends of the setting of paste and concrete with superplasticizers are comparable. That is, SMF-S1 causes the least retardation and PCE-D1 results in higher retardation than SNF-S1 in both paste and concrete.

- The compressive strength increases with an increase in dosage of superplasticizer and is maximum for the highest slump obtained without any segregation or bleeding. This emphasizes the importance of good workability in achieving adequate strength. The decrease in strength observed beyond certain dosage is due to bleeding and segregation.

- The cost of concrete derived from the individual prices of superplasticizer, cement and aggregate shows that low unit cost of superplasticizer need not always result in cost effective concrete. For example, in the studied combinations, even though the unit cost (cost/kg) of SMF-S1 is less than PCE-D1, the former leads to more cost per m^3 of concrete because the dosage of the superplasticizer required for a particular slump is higher for SMF-S1.

8.2.6 Effect of Superplasticizer on the Hydration process and on the Microstructural Development

- Instead of a single technique, multiple techniques (XRD, SEM, thermal methods and Si NMR) have been used complementarily for understanding the effect of superplasticizers on the hydration process and consequently on the microstructure.

- The XRD study gives a qualitative evaluation of the effects of superplasticizers on the hydration. It confirms that the superplasticizer affects hydration and delays the formation of ettringite. In addition to that, it shows that secondary ettringite is present even upto 28 days in some combinations. The evaluation shows that the amount of C-H increases with the age of curing. The presence of C-H peaks at half setting shows that the formation of C-H is not delayed as the formation of ettringite in the presence of the superplasticizers.

- The SEM study shows that the incorporation of a superplasticizer leads to more dense and uniform structure than pure cement paste. However, the amount of unhydrated particles at 3 days in the superplasticized paste is more than that of pure cement paste confirming that the superplasticizer retards the hydration.

- The DTA/TG/DTG analysis also confirms the XRD results that the C-H formation is less affected by the addition of superplasticizers. However, the mass percentage of C-H is very low for a quantitative comparison.

- The NMR results that show that all the superplasticizers studied here decrease the rate of silicate polymerization and lead to a lower amount of polymerized silicates at 3 and 28-days which is indicative of the change in the morphology of C-S-H gel in the presence of superplasticizers.

- As explained in the previous section, the addition of superplasticizer always leads to a slightly higher strength in concrete. However, the physico-chemical analyses indicate that polymerization of silicates is retarded and the amount of C-H formed is lower at early ages. Hence, it can be concluded from the microstructural studies that more uniform and dense structure of superplasticized paste results in slightly higher compressive strength of concrete.

8.2.7 Influence of Chemical Composition of Cement on Compatibility

- Based on this study it is recommended that specification for the alkali content be included in IS code for the chemical composition of cement as the amount of superplasticizer required varies with alkali content; low alkali cement requires more amount of superplasticizer due to more initial adsorption.

- The absorbance study conducted using a UV spectrophotometer shows that it is a good characterization technique for identifying the superplasticizers. This study also suggests that the reason for the increased demand of certain superplasticizers is that there is higher initial adsorption of these superplasticizers.

8.3 Guidelines for Selecting the Best Combination of Cement and Superplasticizer

Based on the present study, a methodology is recommended for the selection of the superplasticizer for concrete mix design. The methodology uses criteria based on the Marsh cone and Vicat penetration tests to select a superplasticizer that is compatible with the cement used. A compatible combination should have a well defined saturation point and the dosage corresponding to the same should be within the manufacturer's recommended limit. Also, the final setting time of superplasticized paste should be less than 16 hours, which is expected to lead to a concrete with a setting time less than 12 hours. However, final trials have to be conducted on concrete to select a cost-effective superplasticizer. The combinations studied here are used to illustrate the evaluation for compatibility based on this methodology, and the results are compared with other approaches in the literature.

8.4 Recommendations for Further Research

The study clarifies many of the conflicting views on the flow behaviour of paste, effectiveness of the Marsh cone test in representing the flow behaviour of the superplasticized paste, the correlation between the flow behaviour of paste and concrete and the influence of superplasticizers on the hardened properties of concrete. Continued research on the following aspects can give better understanding and be of more use to the construction industry:

- The influence of the fines content in the aggregates on the saturation dosage as well as the loss of fluidity with time.

- Regarding the microstructure and hydration processes, the hydration processes could be studied further by incorporating the quantitative measurement of the different phases involved in the hydration through XRD.

- The determination of the Ca/Si ratio of the C-S-H and image analysis of more samples can give a clearer picture of the effect of superplasticizers on the composition of C-S-H and pores in the microstructure. An extensive study on the pore structure of the superplasticized paste is essential for understanding the effect of superplasticizers on the shrinkage of concrete.

- The prediction of the Marsh cone time with the available rheological models is suitable only for a certain range of fluidity. In the cases of pastes with low flow, the models seem to be inappropriate. In addition to that, the viscoelastic characterization shows the change in nature of the paste from non-linear viscoelastic to viscous with variation in the type and dosage of superplasticizer. Hence, an appropriate constitutive model is required for the whole range of flow.

- The interaction of the superplasticizer with mineral admixtures and VMA requires further study for the optimization of paste as well for understanding the loss of fluidity. In addition, the influence of other admixtures like shrinkage reducing and accelerators on the cement-superplasticizer interaction need further attention.

- Absorbance based studies of superplasticizer adsorption can be extended for understanding the influence of mineral admixtures and VMAs on the amount and rate of adsorption of superplasticizers on cement surface which in turn affects the loss of fluidity. The zeta potential of different pastes could be measured for validating the adsorption study.

Finally, the number of tests on fresh cement paste are quite satisfactory for definite conclusions to be made whereas in the studies performed on hardened cement paste, the number of tests has been quite limited, which makes unambiguous conclusions difficult. Therefore, more extensive tests can be performed on the properties of hardened concrete for confirming the trends seen in paste.

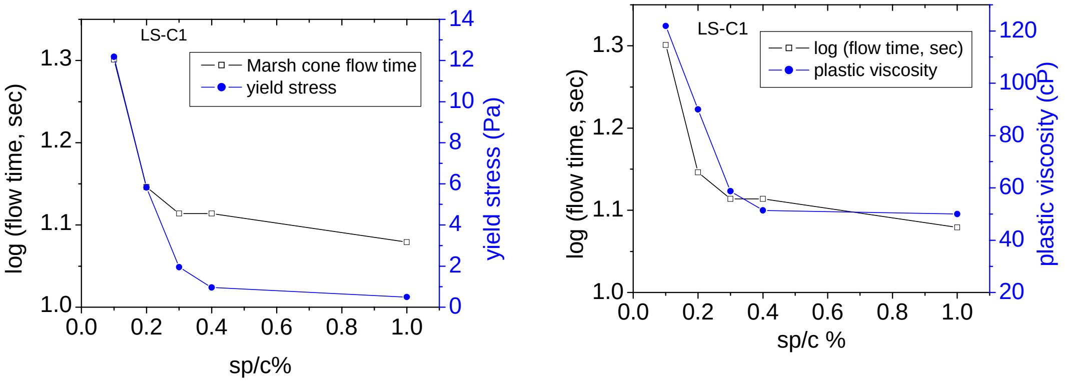
APPENDIX A

Table A.1 Test results of three trials in the selection of mixing method

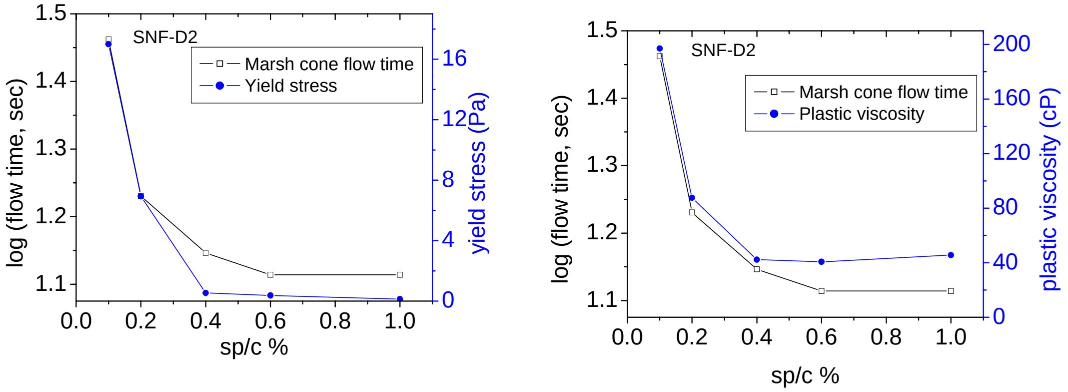
Type of mixing	Optimum superplasticizer dosage (sp/c%)		
	trial 1	trial 2	trial 3
Hobart with B-flat beater	0.10	0.13	0.09
Hobart with D-wire whip	0.19	0.16	0.12
Blender	0.13	0.14	0.16
Grinder	0.15	0.16	0.07
Hand	0.39	0.20	0.06
Ball mill mixing (steel balls)	0.07	0.16	0.11
Ball mill mixing (Glass marbles)	0.15	0.16	0.14

Table A.2 Comparison of superplasticizer dosages
(data from Marsh cone and viscometer tests)

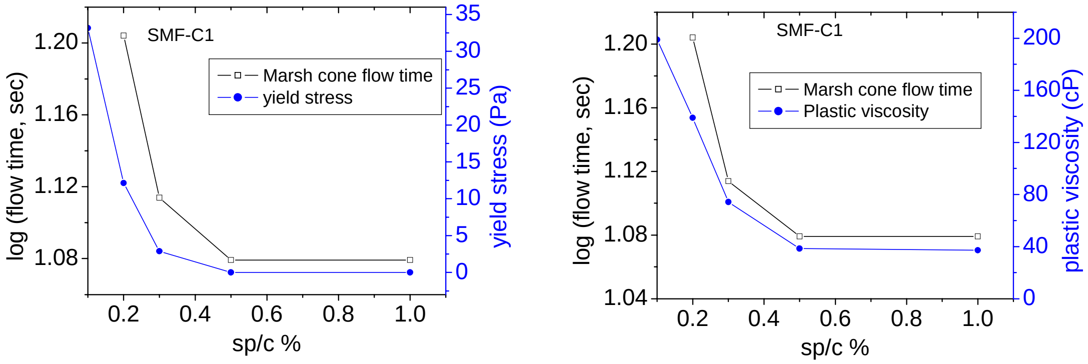
Super-plasticizer	Dosage for constant yield stress	Dosage for constant plastic viscosity	Optimum dosage corresponding to 140° (at 0 minutes)	Dosage corresponding to 140° (at 60 minutes)	Dosage from Aïtcin method using flow-time curves at 0 and 60 minutes
LS-C1	0.4	0.4	0.25	0.26	0.3
SNF-S1	0.3	0.3	0.20	0.34	0.3
SNF- D1	0.4	0.5	0.24	0.23	0.3
SNF-D2	0.4	0.4	0.23	0.46	0.4
SNF- C1	0.3	0.3	0.16	0.20	0.3
SMF-S1	0.3	0.3	0.23	0.30	0.5
SMF-C1	0.5	0.5	0.20	0.30	0.5
PCE-S1	0.3	0.3	0.20	0.24	0.4
PCE-D1	0.1	0.1	0.07	0.17	0.2



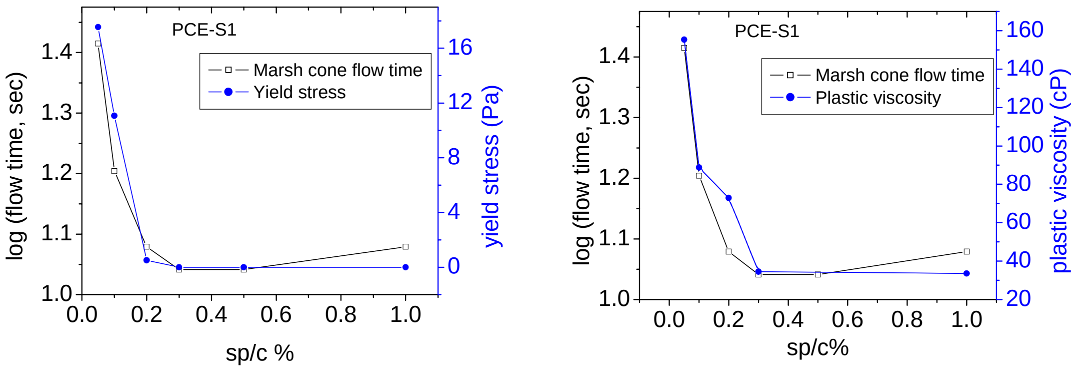
(a) Correlation between Marsh cone flow time and rheological parameters for LS-C1



(b) Correlation between Marsh cone flow time and rheological parameters for SNF-D2

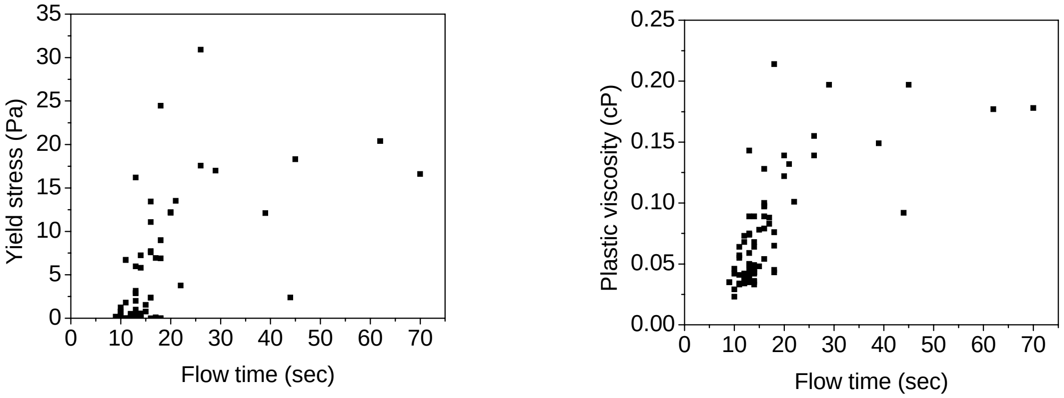


(c) Correlation between Marsh cone flow time and rheological parameters for SMF-C1

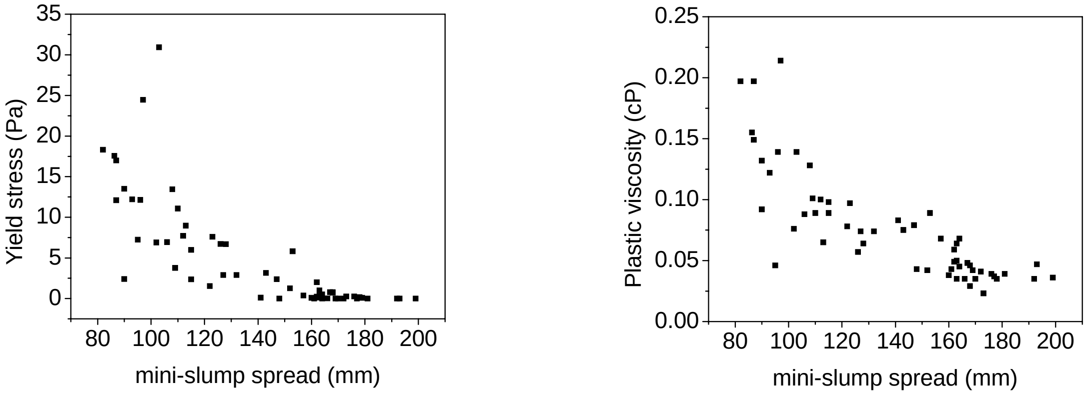


(d) Correlation between Marsh cone flow time and rheological parameters for PCE-S1

Fig. A.1 Correlation between Marsh cone flow time and rheological parameters of superplasticizers



(a) Correlation between Mash cone flow time, yield stress and plastic viscosity for different combinations



(b) Correlation between Mini-slump spread, yield stress and plastic viscosity for different combinations

Fig. A.2 Correlation between Marsh cone flow time and mini-slump spread with rheological parameters for different compositions

APPENDIX B

Matlab programme to calculate flow time as per Nguyen model

```
%to calculate the velocity at the exit of the nozzle
%to calculate the time for falling the level from h1 to h2
clc
n=input('enter value of n =  ');
R=0.004;
rho=input('enter value of rho =  ');
g=9.81;
H=0.06;
tanphi=0.267;
lamda=0.96;
tuo0=input('enter value of tuo0 =  ');
k=input('enter value of k =  ');
alpha1= (1-(1.1*(tuo0/(rho*g*H*tanphi))));
alpha2=(1+(R/(3*n*H*tanphi)));
alpha=alpha1/alpha2;
syms x real
deltap=((alpha*rho*g)*(1+x/H)-rho*g)*H;
r0=2*tuo0/(rho*g+(deltap/H));
f1=1+((2*n)/(2*n+1))*(r0/R);
f2=((2*n^2)/((n+1)*(2*n+1)))*(r0/R)^2;
f3=(1-(r0/R))^((n+1)/n);
f=(f1+f2)*f3;
v1=n*R/(3*n+1);
v2=(alpha*rho*g*R)/(2*k);
v3=(H+x)/(H);
v=(v1*(v2*v3)^(1/n))*f;
Re=(rho*((v)^(2-n))*(2*R)^n)/k;
B1=(1/(2*lamda))*sqrt((alpha*R)/H);
B2=(n/(2*(3*n+1)))^(n/2);
B3=(1-(exp(-0.1*sqrt(Re))));
B4=(sqrt(Re)+(1.5/n)*(Re^(1/4)));
B=(B1*B2*B3*B4)+1;
vb= v/B;
t1=(R+(x*tanphi))^2;
```

```
t2=(vb)*R^2;
t3=t1/t2;
ii=linspace(0.224,0.165,100);
stepsize=ii(2)-ii(1);
for jj=1:length(ii)
fval(jj)=subs(t3,ii(jj));
end
cumsum=0;
for jj=2:length(ii)
cumsum=cumsum+(fval(jj)+fval(jj-1));
end
time=-((stepsize/2)*cumsum)
```

APPENDIX C

INFLUENCE OF SUPERPLASTICIZER ON THE NON-NEWTONIAN CHARACTERISTICS OF CEMENT PASTE

C.1 GENERAL

The superplasticized cement paste usually exhibits non-Newtonian characteristics, which depend on the type of superplasticizer and its dosage. The superplasticizer causes an increase in the fluidity of the paste and shear thinning behaviour as explained in Chapter 3. However, in some instances of incompatibility, excessive amount of superplasticizer is added, which can result in possible shear thickening. This shear thickening may be due to high concentration of solids in nonflocculated suspensions as the hydration process is accelerated during shearing (Struble and Sun 1995; Cyr et al. 2000). Also, an agglomeration of excessive amount of superplasticizer available in the solution causes more elasticity and possible shear thickening (Papo and Piani 2004).

Typically rotational viscometers have been used for characterizing the rheological behaviour of cement paste as explained earlier (Roy and Asaga 1979; Masood and Agarwal 1994; Ferraris et al. 2001; Park et al. 2005; Schwartzentruber et al. 2006). Most of these investigations subject the material to a cycle consisting of shear rate increasing and decreasing in a stepwise manner. Normally the cycles are repeated and the shear stress-shear rate relationship in the down ramp of either the first, second or third cycle is considered for further analysis (Papo and Piani 2004; Roussel and Roy 2005). Current attempts in the cement paste rheology literature have mainly focused on reducing the data from steady shear experiments to standard constitutive models, and exploring the influence of superplasticizer dosage and type based on these model parameters as seen in

Chapter 3. A variety of models such as Bingham, Herschel- Bulkley, Power law models etc., are used for characterizing the response of the material. The main intent of most of these investigations have been to study the influence of these admixtures on some of these model based parameters such as plastic viscosity, yield stress, consistency, flow index etc. For instance, the influence of the dosage of superplasticizer on the Bingham model parameters like yield stress and plastic viscosity shows that both of these parameters decrease with increase in dosage of superplasticizer up to saturation dosage and remains constant thereafter (Asaga and Roy 1980; Banfill 1981; Nehdi and Rahman 2004). Similar is the case with Herschel-Bulkley parameters like yield stress, consistency and consistency index (Atzeni et al. 1985; Nehdi and Rahman 2004). There are also contradictory observations reported in the literature for the same mixture of materials. For instance, while the Bingham model reports negative yield stress for high dosage of superplasticizers, Herschel-Bulkley model reports a non–negative yield stress and the reason for this is normally ascribed to the so called non-linearity between shear stress and shear rate of Herschel-Bulkley model (de Larrard et al. 1998).

As discussed earlier, the cement paste during the pre-induction period can exhibit shear thinning when sheared in a coaxial viscometer. The rate at which the shear thinning characteristic of the material changes depends on the time at which the material is sheared. After pre-induction period, the same material can exhibit shear thickening behaviour. The scenario is more complex for the superplasticizer-cement paste mixture. Issues such as compatibility/incompatibility and low and high dosage change the rheological behaviour considerably (Mailvaganam 1999). A compatible system at a low dosage of superplasticizer normally will keep the cement particles in a state of dispersion even up to 60 minutes (Agullo et al. 1999). This can be observed by the more or less

Newtonian behaviour in steady shear experiment, in a rotational viscometer. However if the same material is sheared in a dynamic shear rheometer it is possible for it to exhibit high normal stress differences thus conclusively proving the non–Newtonian response characteristics (Mansoutre et al.1999; Min et al. 1994). Also, the same material can exhibit creep and recovery and stress relaxation behaviour thus showing a viscoelastic material response (Struble and Schultz 1993; Sun et al., 2006).

Significant insight into the nature of cement paste has been gained recently due to the investigations of Van Damme et al. (2002). Essentially one can visualize the paste as a dense assembly of deformable or rigid objects close to a jamming situation. These dense assemblies are lubricated by the hydrodynamic or physical-chemical interactions of the interstitial fluid, a mixture of water and superplasticizer. One important aspect of pastes when viewed as an assemblage of granular particles is the property of dilatancy. Essentially, pastes when subjected to shear strain will exhibit the tendency to expand in the direction perpendicular to the shear plane. In a typical dynamic shear rheometer experiment where the gap between the two plates is kept fixed, this essentially results in the development of normal stresses. Van Damme et al. (2002) postulate that the two important properties that give complete description of the mechanical behaviour of the paste is the effect of dilatancy and inter-granular friction; the latter described very closely by the 'yield stress'. They used these concepts to study the rheological behaviour of flocculated calcium silicate pastes and emphatically observe the need to measure normal force in shear flow in addition to the 'yield stress' for a complete characterization of superplasticized cement paste.

A proper constitutive model taking into account all the internal structural changes taking place during the hydration process is lacking currently. This is not surprising as the cement paste-superplasticizer mixture exhibits diverse and complex response characteristics. However, even before one attempts in building a constitutive model, it is imperative to understand through careful experimental investigations the transition in the viscometric properties over a period of time. This information is necessary in building a proper constitutive model. The intent of this investigation is precisely that.

It has been observed that the Marsh cone is extensively used in the optimization of high performance concrete mixture design (see Chapter 3). Since the idea of using superplasticizer is to impart linearly viscous behavior for a short period of time to the paste and the mixture, the flow time measured in a Marsh cone has been linked to the superplasticizer dosage beyond which there is no appreciable change in flow time is normally taken as the optimum dosage. There are several interesting issues related to this aspect. First, for a given cement paste – superplasticizer mixture, the optimum dosage essentially relates the transition from a non-Newtonian to a Newtonian behavior. If one assumes the Bingham model for the cement paste – superplasticizer mixture for dosages less than the optimum dosages, the equations to be solved are the Buckingham-Reiner equation and for the dosage equal to and greater than the optimum dosages, the classical Hagen-Poiseuille equation are required to be solved. Also, discussions in the earlier paragraphs clearly indicated that it is possible for the cement paste – superplasticizer mixture to exhibit shear thickening, a typical non-Newtonian behavior for over dosage. Hence, it is expected that the flow time might start increasing beyond the optimum dosage as seen in the Chapter 3. It is also to be noted that this optimum dosage may not be a sharp transition point, it is normally asymptotic in nature and hence it will be natural that there can be several dosages near the optimum dosage which will result in the transition from non-Newtonian to Newtonian. It will also be helpful if this transition point is arrived at by appealing to kinematics of fluid flow rather than inferring it through model dependent parameters.

In this investigation, several combinations of cement paste and superplasticizer are tested in a Brookfield viscometer (details are given in Chapter 3) and Anton Paar dynamic shear rheometer. The raw experimental data in terms of torque - shear stress – shear rate are examined and detailed analysis is made on the various interesting manifestations of the rheology of cement paste. The main thrust here is that the non-Newtonian behavior of cement paste and superplasticizer mixture is characterized based on more fundamental experimental investigations without recourse to any specific model. Steady shear experiments, creep and recovery and stress relaxation experiments were conducted on a variety of superplasticizer and cement paste combinations and the transition from non-linear viscoelastic to non-Newtonian to linearly viscous fluid as the dosage rate is increased is captured. Additionally the saturation dosages obtained from Marsh cone tests were compared and it was found that dosage rates determined using Marsh cone were closer to the dosage rates where the transition to the linearly viscous fluid was seen.

C.2 Materials used

The physical and chemical characteristics of cement and four types of superplasticizers used for the study are same as given in Section 3.2

Table C.1–Mix details for steady shear experiments

Type of superplasticizer	Dosage of superplasticizer (sp/c %)	Saturation dosage of superplasticizer from Marsh cone test (sp/c %)
SNF-S1	0.1, 0.2, 0.3, 0.4, 1	0.20
SNF-D2	0.1, 0.2, 0.4, 0.6, 1	0.23
SMF-S1	0.1, 0.2, 0.3, 1	0.23
PCE-D1	0.05, 0.1, 0.2, 0.4, 1	0.07

C.3 Experimental Procedure

The mixing procedure for the preparation of the paste is same as given in Section 3.5.The Marsh cone test was used to evaluate the relative fluidity and the saturation superplasticizer dosage. Table 1 gives The saturation superplasticizer dosages for the four products used in this study are given in Table C.1. The details of the steady shear experiments using Brookfield HA DV II +pro were explained in detail in Section 3.5. The rheological experiments were also conducted with an Anton Paar dynamic shear rheometer for studying the creep and recovery, and stress relaxation responses. The tests were conducted with a parallel plate attachment with a gap of 1 mm (see Figure C.1). The details of these tests are given in the respective sections that follow.

Fig. C.1(a) Anton Paar Rheometer (b) Shearing of cement paste with parallel plate attachment

C.4 Results and Discussions

C.4.1 Marsh cone test on pastes

The saturation dosages obtained from Marsh cone test results for four superplasticized pastes, already presented in Chapter 3, are summarized in Table C.1.

C.4.2 Steady shear tests with viscometer

Superplasticized cement paste generally shows shear thinning behaviour with an increase in shear rate. This is due to the breakdown of the hydrated products formed around the cement grain due to continuous mixing leading to the reduction in the apparent viscosity. During unloading apparent viscosity remains constant during the down curve of the hysteresis cycles for the PCE based product as shown in Figure C.2. It is observed that the area within the loop decreases from the first cycle to the second cycle, because the energy required for breaking down the hydration products decreases with time.

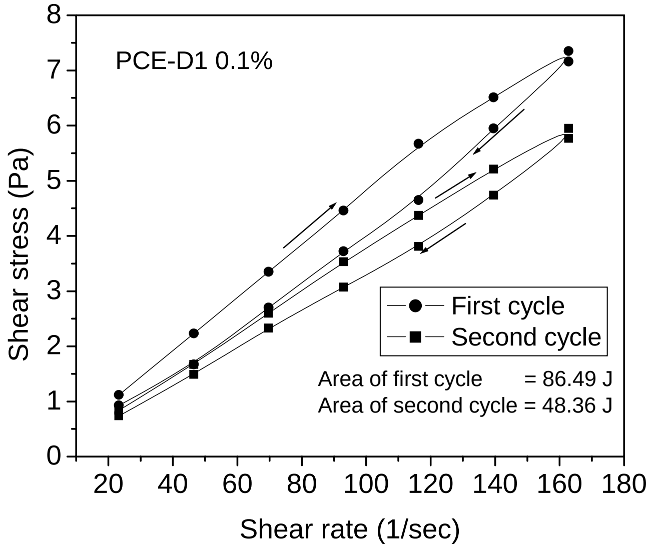


Fig. C.2- Loading-unloading cycles for the superplasticizer PCE-D1 at the dosage of 0.1%

Viscometric test results on paste shows that the behaviour changes from shear thinning nature to Newtonian and shear thickening depending on the type and dosage of superplasticizer (Lootens et al. 2004; Papo and Piani 2004; Chen et al. 2006). The reported results on shear thickening are mainly based on oscillatory tests in terms of storage modulus and viscous modulus (Chen et al., 2006; Chougnet et al. 2007). The model parameters derived from viscometric tests and hysteresis cycles are used to capture the change from shear thinning to shear thickening behaviour in Chapter 3.

The shear thinning and thickening nature of materials can also be classified based on the area within the loading-unloading cycle as it reflects the energy required for breaking down of the structure of the paste. Figures C.2 and C.3 show the work done in deflocculating the particles for shear thinning and shear thickening compositions, respectively. The area in the loop decreases from the first cycle to the second cycle for shear thinning material because the energy required for breaking down of the particles decreases. In the case of shear thickening material, the area within the loop increases.

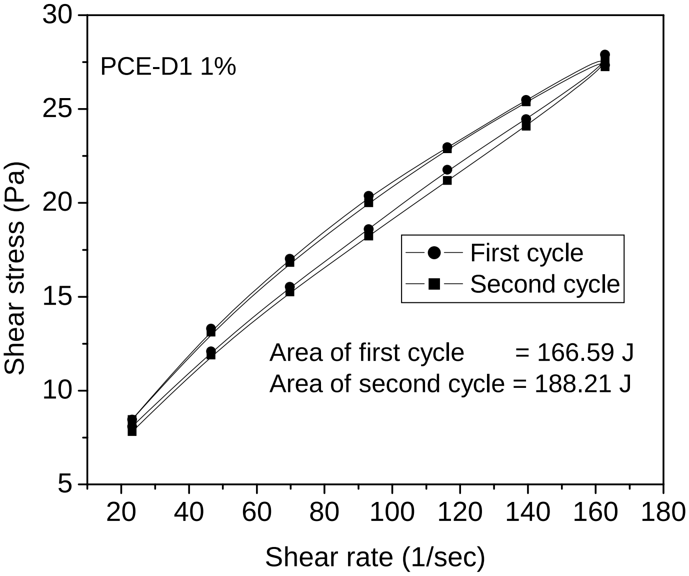


Fig. C.3- Loading-unloading cycles for the superplasticizer PCE-D1 at the dosage of 1%

Table C.2 shows the areas within the loading-unloading loops for the different pastes studied, along with the saturation dosages for different compositions and it can be seen that more work is required at low dosages of superplasticizer to make the paste to flow, and that the area of the loops decreases with an increase in the dosage of superplasticizer.

It can be observed that the area calculation is reliable upto the saturation dosage of superplasticizer and the maximum percentage reduction occurs approximately at the saturation dosage of superplasticizer. The paste with PCE-D1 shows shear thickening at 1% and hence work required for structural breakdown increases with time of shearing. Thus, the reduction in the area of hysteresis cycles indicates the effectiveness of different superplasticizers as it represents the amount of work required to deflocculate the particles. From the perspective of rheology of cement paste-superplasticizer mixture, this reduction in area is related to the transition from non-Newtonian to Newtonian regime. However, the trend is not clear in other superplasticizers.

Table C.2 Work done in different loading-unloading cycles

Type of SP	sp/c %	Saturation dosage (sp/c%)	Loop area of first cycle (N/m^2s)	Loop area of second cycle (N/m^2s)
SNF-S1	0.1	0.20	234	230
	0.2		108	92
	0.3		28	3
	0.4		85	65
	1		44	7
SNF-D2	0.1	0.23	667	356
	0.2		115	55
	0.4		143	135
	0.6		140	135
	1		124	112
SMF-S1	0.1	0.23	672	299
	0.2		81	41
	0.3		118	58
	1		130	85
PCE-D1	0.05	0.07	1813	820
	0.1		86	48
	0.2		91	22
	0.4		37	24
	1		167	188

C.4.2.1 Shear thinning index

Superplasticized paste exhibits shear thinning nature as the structural breakdown is faster than structural build up. The degree of shear thinning of non Newtonian fluids for different combinations can be represented by the shear thinning index (ASTM D 2196 (2005)); the shear thinning index is defined as the apparent viscosity at low speed to that at high speed. Accordingly, in this case the shear thinning index is calculated based on the apparent viscosity at 25 rpm and 175 rpm.

Table C.3 shows the influence of the type and dosage of superplasticizer on the shear thinning index. Higher the shear thinning index, higher is the degree of shear thinning. It is observed that generally the shear thinning index decreases with an increase in the dosage of superplasticizer, which shows that the effect is predominant at low dosages. PCE D1 shows considerable shear thinning even at low dosages and at overdosage, causes some shear thickening (i.e., shear thinning index is less than 1). For all compositions, shear thinning occurs upto the saturation dosage and after that the index remains almost constant. The shear thinning index of less than one in all cases shows that the apparent viscosity at high shear rate is slightly higher than that at low shear rate. This generally occurs at overdosage of superplasticizer because of the excess amount of superplasticizer available in the solution which forms a network. Hence, it is proposed that the shear thinning index of one can be used as a limit for the dosage of the superplasticizer. Interestingly, the dosage corresponding to this limit is practically comparable with the saturation dosage obtained with Marsh cone and coaxial cylinder viscometer (except SNF-D2). In the case of PCE based superplasticizer, a small increase in dosage of 0.05% causes a large reduction in the shear thinning index, showing its effectiveness at low dosages.

Table C.3 Shear thinning indices for different types and dosages of superplasticizers

Type of superplasticizer	Dosage of SP	Shear thinning index
SNF-S1	0.1	4
	0.2	3
	0.3	2
	0.4	1
	1	1
SNF-D2	0.1	3
	0.2	3
	0.4	1
	0.6	1
	1	1
SMF-S1	0.1	3
	0.2	3
	0.3	2
	1	1
PCE-D1	0.05	3
	0.1	1
	0.2	1
	0.4	1
	1	1

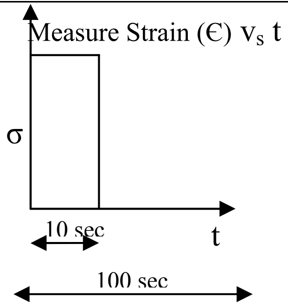
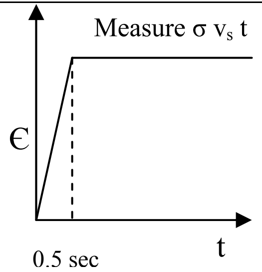
C.4.3 Creep and Recovery and Stress Relaxation Experiments

The behaviour of cement pastes under steady shear has been determined using different procedures (Lapasin et al. 1979; Lapasin et al. 1983; Atzeni et al. 1995; Geiker 2002). These studies explain that the material behaviour changes from solid-like to fluid-like with the variation of shear stress with time. They consider the yield stress as a criterion for the change of material behaviour. The concept of 'yield stress' is discussed in detail in the excellent review article by Barnes (1999) which also discusses various issues related to whether 'yield stress' is a model derived parameter or a true phenomenon. In the present study, tests were conducted with an Anton Paar rheometer using five different compositions - pure cement paste and cement paste with four types of superplasticizers to understand the influence of different superplasticizers on the flow behaviour (see Table C.4). The details of the testing methods are given in Table C.5.

Table C.4 Mix details for creep and recovery and stress relaxation experiments

Composition of paste	w/c	Dosage of superplasticizer (sp/c%)
Pure cement paste	0.35	Nil
Cement paste with SNF-S1	0.35	0.05, 0.20
Cement paste with SNF-D2	0.35	0.05, 0.23
Cement paste with SMF-S1	0.35	0.05, 0.23
Cement paste with PCE-D1	0.35	0.01, 0.025, 0.05, 0.07, 0.1

Table C.5 Details of the different data acquisition frequencies

Details of test	Number of data points	Measuring point duration	Testing details
1. Creep and Recovery Creep (10 sec) Recovery (100 sec)	 200 40	 0.05 sec 0.05 to 5 sec varied linearly during 100 sec	
2. Stress relaxation Ramping of strain (0.5 sec) Stress relaxation (33 sec)	 100 10	 5×10^{-3} sec 5×10^{-3} sec to 20 sec varied logarithmically during 33 sec	

C.4.3.1 Creep and Recovery Test on Cement Paste

Most flow studies of paste and models used consider the material as viscous only. In this section an attempt is made to observe whether the material shows any viscoelastic nature and whether the addition of superplasticizer results in a transition to non-Newtonian behaviour.

Struble and Leit (1995), and Struble and Schultz (1993) demonstrated that creep and recovery behaviour of cement paste undergoes a transition from solid-like behaviour at low stress to fluid like behaviour at high stress. However, at high stress, the material behaves as a viscous liquid with a linear increase in strain throughout the duration of stress with no recovery. This stress level associated such a transition agrees with the yield stress estimated from flow curves and oscillatory tests in their study. Creep and recovery tests have also been used to monitor the setting of cement paste based on the development of yield stress with time (Struble and Leit 1995).

Generally, in a stress controlled test, when the material is subjected to instantaneous stress followed by a constant stress, an instantaneous increase in strain occurs initially and then there is a continuous increase in strain at a non-constant rate, i.e., an elastic response followed by combination of elastic and viscous response. If the material is fluid-like, the strain rate asymptotically approaches a constant value. While releasing the stress, some instantaneous strain recovery followed by delayed recovery occurs (Wineman and Rajagopal, 2000).

In the present study, creep and recovery tests were done on pure cement paste and superplasticized cement pastes. Tests were conducted at different stress levels in order to understand how the nature of the material changes at different stress levels for different types of superplasticizers and dosage rates. Figure C.4 shows the test results for pure cement paste, which shows a typical viscoelastic nature with some residual strain at different stress levels. The stress levels used include 50 Pa, 75 Pa and 100 Pa and it can be observed that the strain produced at higher stress levels is higher. Also, the recovery is less for lower stress.

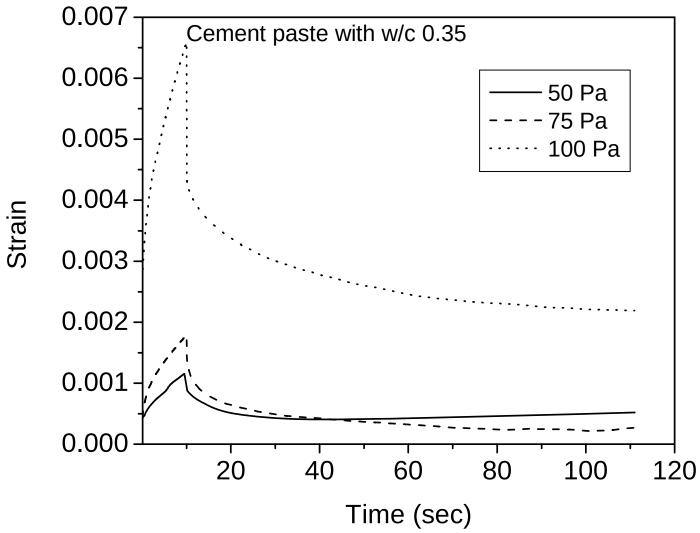
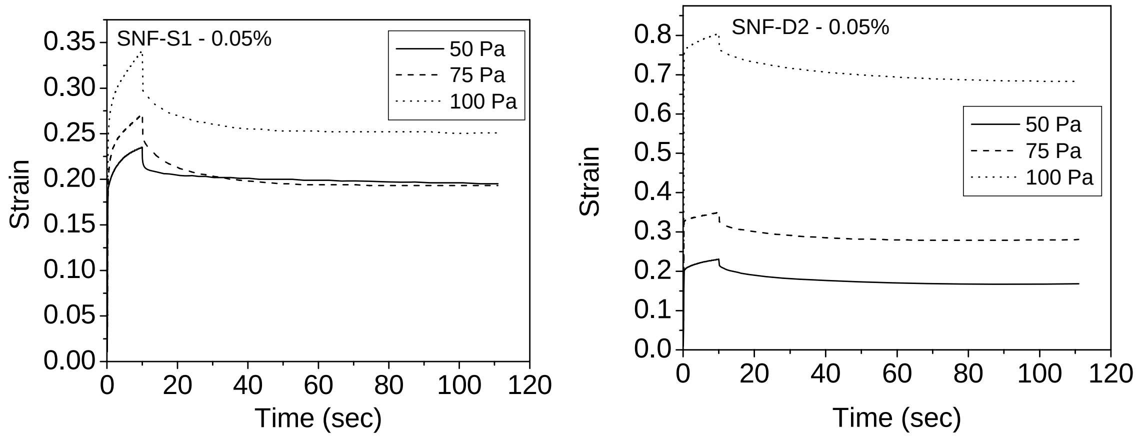


Fig. C.4 Creep and recovery test for pure cement paste

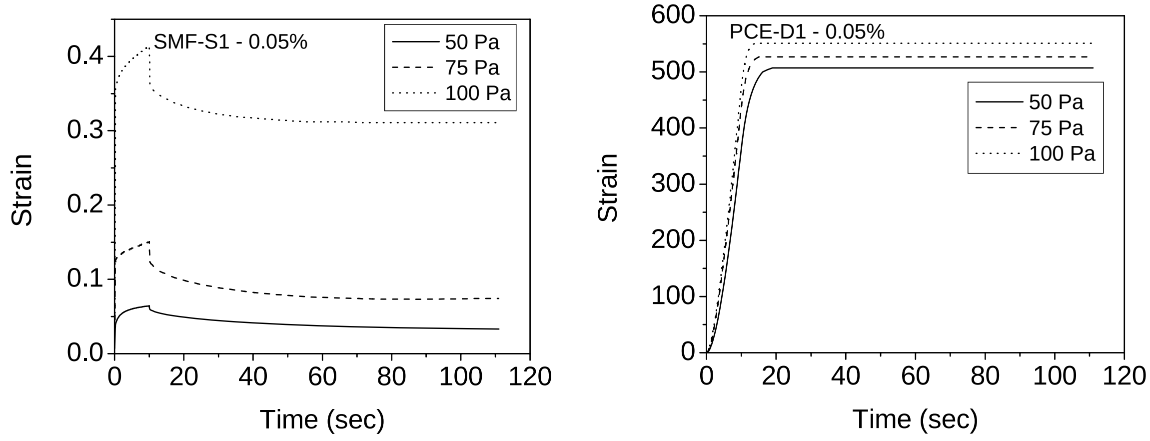
Influence of type of superplasticizer on creep and recovery

Figure C.5 (a-d) shows the influence of types of superplasticizers on the rheology of cement paste. Tests were conducted for four superplasticizers (see Table C.4) at constant dosage of 0.05%. the pastes with the SNF and SMF based superplasticizers show the same trend as the pure cement paste; however, strain recovery is less compared to pure cement paste. Moreover, the cement paste with PCE based superplasticizer shows an entirely different nature. It shows linear strain initially and no instantaneous strain or recovery. This is because the paste becomes viscous at that dosage due to the better dispersion produced by the combined action of electrostatic repulsion and steric hindrance.



(a) Creep and recovery of SNF-S1

(b) Creep and recovery of SNF-D2



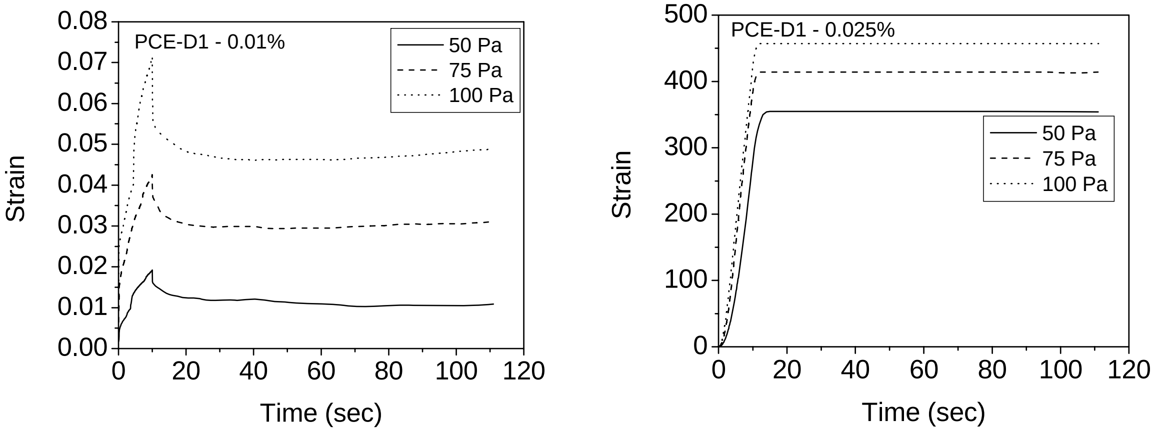
(c) Creep and recovery of SMF-S1

(d) Creep and recovery of PCE-D1

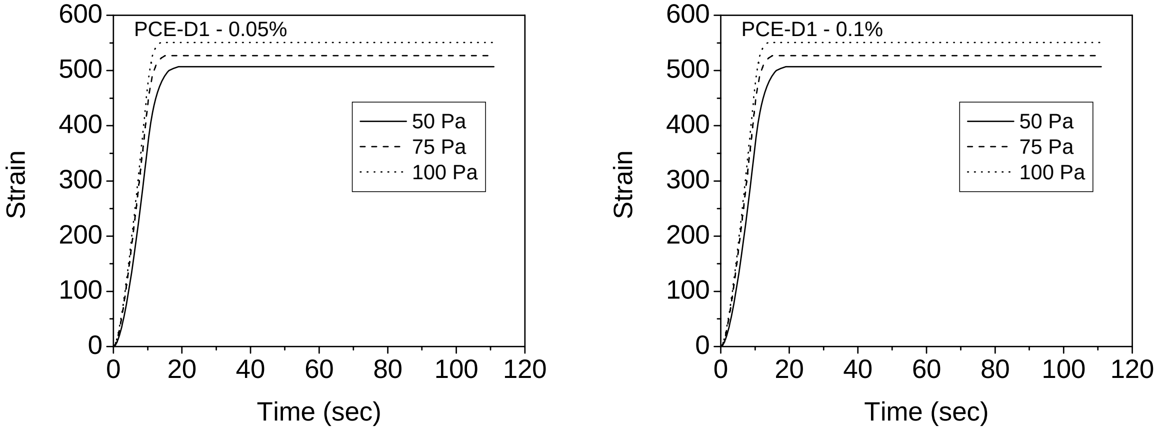
Fig. C.5 (a-d) Creep and recovery test result of cement paste and with constant dosage of different superplasticizers

Influence of dosage of superplasticizer on creep and recovery

In order to understand the influence of dosage of superplasticizer on creep and recovery, tests were conducted with the most effective superplasticizer PCE-D1 (determined from Marsh cone test) at different dosages. The test results are given in Figure C.6 (a-c). It is observed that the nature of the paste changes from viscoelastic to viscous as the dosage of superplasticizer increases from low to saturation. Also, the strain/deformation of the material increases with an increase in dosage of superplasticizer.



(a) Creep and recovery of PCE-D1, 0.01% (b) Creep and recovery of PCE-D1, 0.025%

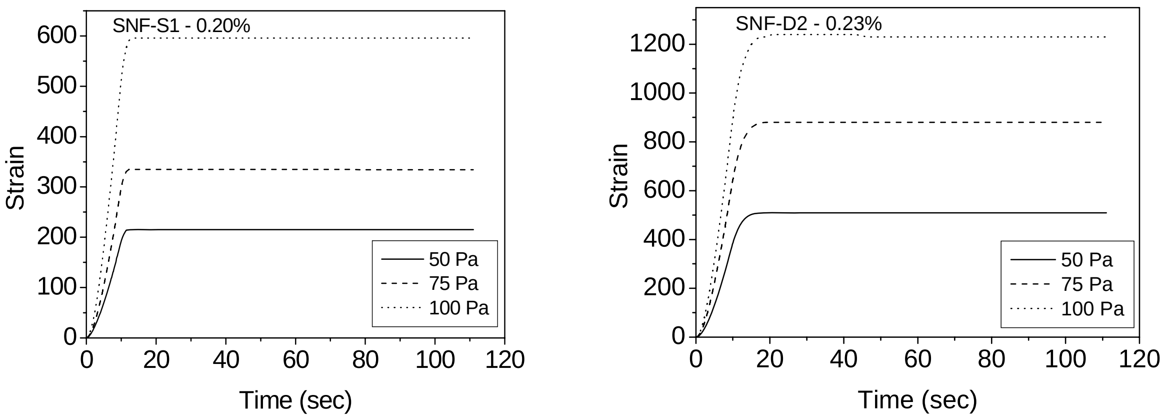


(c)Creep and recovery of PCE-D1, 0.05% (d) Creep and recovery of PCE-D1, 0.1%

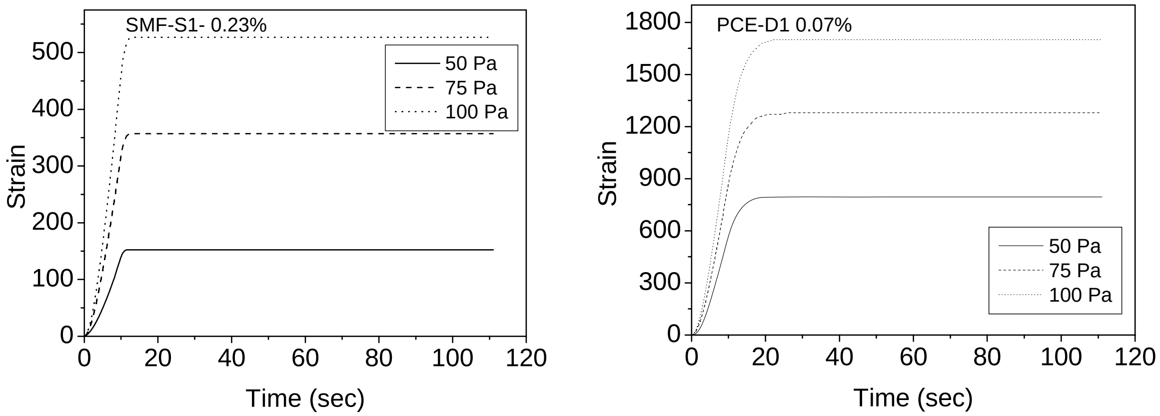
Fig. C.6 (a-d) Variation in creep and recovery behaviour
with different dosages of PCE-D1

Influence of saturation dosage of superplasticizer on creep and recovery

A comparison of the flow behaviour of pastes was obtained by conducting creep tests at the saturation dosage of superplasticizers (see Figure C.7 (a-d)). It is observed that all pastes show a viscous nature with a linear increase in strain initially and no recovery while releasing the stress at their saturation dosages. Thus a transition in the nature of material occurs at saturation dosages, which is necessary to have a flowable concrete at the saturation dosages.



(a) SNF-S1, at saturation dosage, (b) SNF-D2, at saturation dosage ,



(c) SMF-S1, at saturation dosage , (b) PCE-D1, at saturation dosage

Fig. C.7 (a-d) Creep test result at saturation dosage of superplasticizers

Check for linearity of response

The simplest modeling concept for viscoelastic materials for which the experimental data can be characterized is called linearity of response (Wineman and Rajagopal, 2000). It consists of two conditions (1) linear scaling and (2) superposition of separate responses. If the response of a viscoelastic material displays both linear scaling and possibility superposition of separate responses for all histories, the response is said to be linear. If the stress (σ_0) is changed by a factor α, and if the deformation is also changed consequently by the same factor α, then the material shows linear scaling. In our current investigation, the stress levels are 50 Pa, 75Pa and 100Pa and for checking linear response, 50 Pa is multiplied by a factor of 1.5 and 2. If the material satisfies linear scaling, the deformation response obtained by increasing the stress by these factors should be same as that of the deformation produced by 75 Pa and 100 Pa respectively. However, Figure C 8 (a and b) shows that the pure cement paste as well as that with superplasticizer at a low dosage, violate the condition of linear scaling in the tested compositions. The same behavior was found for all the combinations tested.

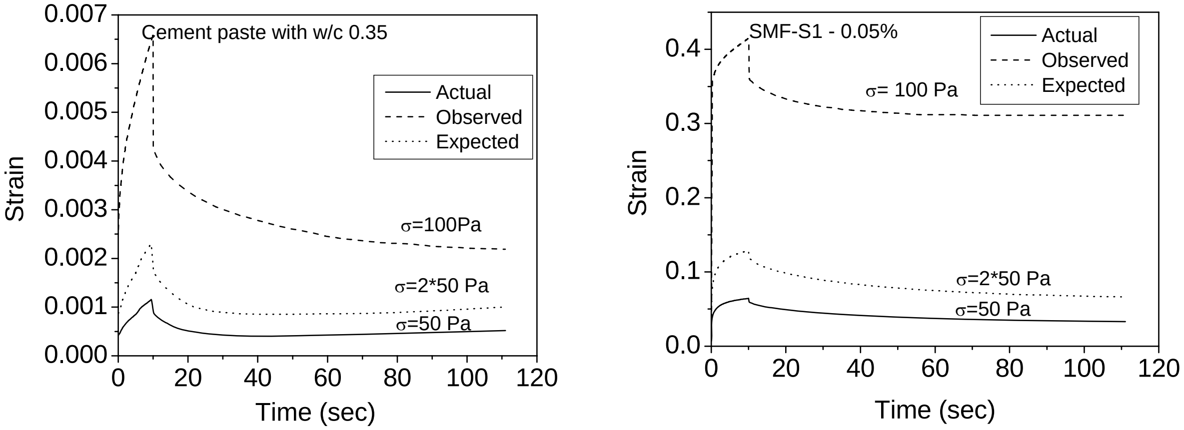


Fig. C.8 Test for linear scaling

If the material follows the principle of superposition, then the instantaneous deformation due to the applied load at time t = 0 and the instantaneous deformation recovered on the release of the load should be same. The instantaneous deformation due to loading and instantaneous deformation due to unloading as observed from above Figure C.8 and Table C.6 at a dosage of 0.05%, are different. This shows that the cement paste tested in this investigation also violates the condition of superposition of separate responses. These two checks show that pure cement paste and superplasticized pastes have a non-linear viscoelastic nature at dosages less than saturation. However, the recovery could not be observed for superplasticizers at saturation dosages.

Table C.6 Superposition of separate responses

Composition	Stress (Pa)	Instantaneous Strain on loading	Recovered strain on unloading
Cement paste	50	0.00037	0.000171
	75	0.00038	0.00017
	100	0.0026	0.00114
Cement paste with SNF-S1	50	0.0107	0.0015
	75	0.0119	0.003
	100	0.0147	0.0045
Cement paste with SNF-D2	50	0.0098	0.002
	75	0.0141	0.003
	100	0.0214	0.0035
Cement paste with SMF-S1	50	0.0072	0.0014
	75	0.0141	0.003
	100	0.0171	0.0045
Cement paste with PCE-D1	50	0.0127	0
	75	0.0194	0
	100	0.0254	0

C.4.3.2 Stress Relaxation

In the case of a viscoelastic material, when strain is instantaneously increased at t = 0 and then maintained, the stress instantaneously increases and then gradually decreases with time. Tests are conducted on different compositions as described in creep and recovery tests. In the case of pure cement paste, the material shows viscoelastic nature as the stress reduces asymptotically to zero (see Figure C.9).

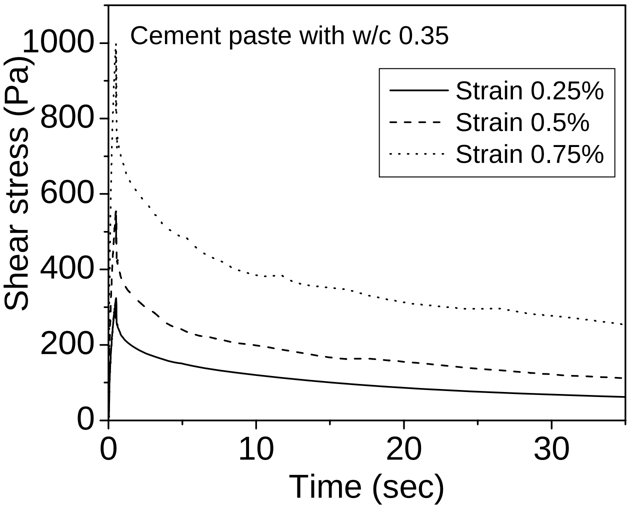
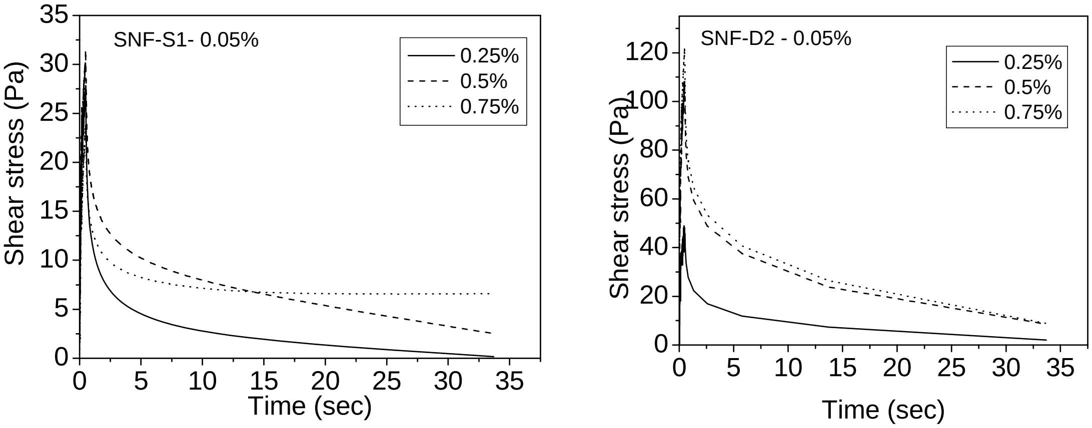


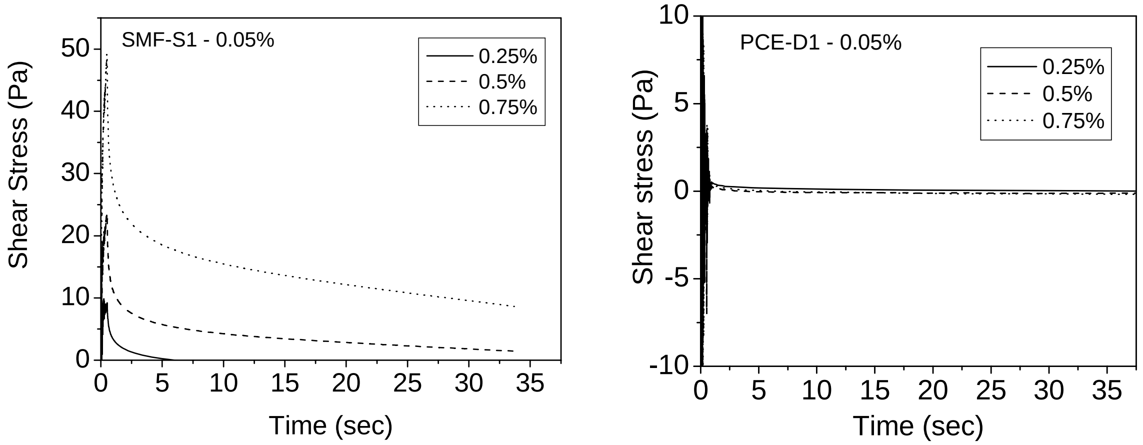
Fig. C.9 Stress relaxation of pure cement paste

Influence of type of superplasticizer on stress relaxation

Figure C.10 (a-d) shows stress relaxation test results for different types of superplasticizers at a constant dosage of 0.05%.The SNF and SMF based superplasticizers show viscoelastic nature as in the case of pure cement paste. In the case of PCE based paste, no external force is required to maintain the strain because the dosage is high enough to ensure fluid-like behaviour. This is because of the better dispersion produced due to PCE based superplasticizer.



(a) Stress relaxation of SNF-S1 (b) Stress relaxation of SNF-D2

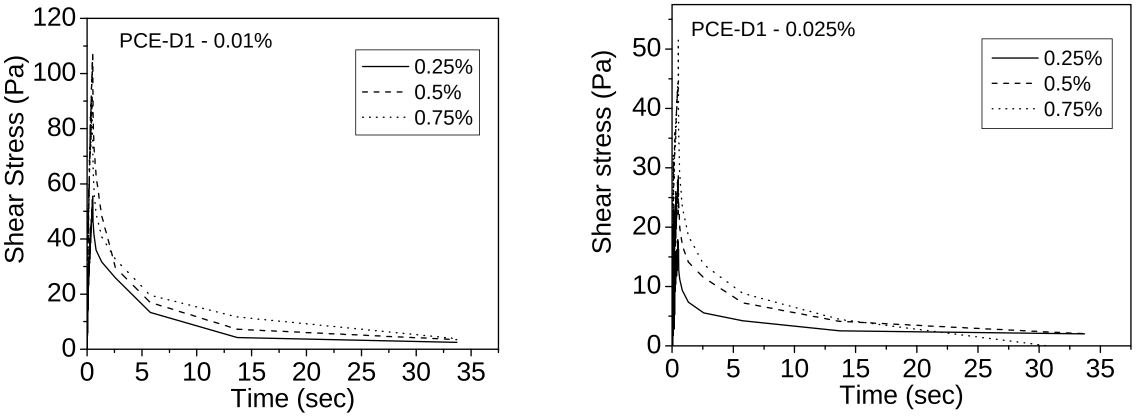


(c) Stress relaxation of SMF-S1 (b) Stress relaxation of PCE-D1

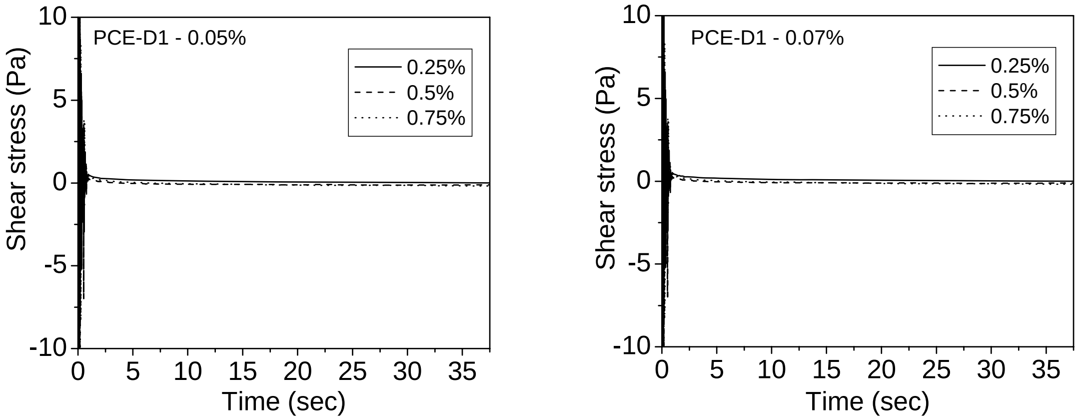
Fig. C.10 (a-d) Stress relaxation test results for pastes with 0.05% dosage for different superplasticizers

Influence of dosage of superplasticizer on stress relaxation

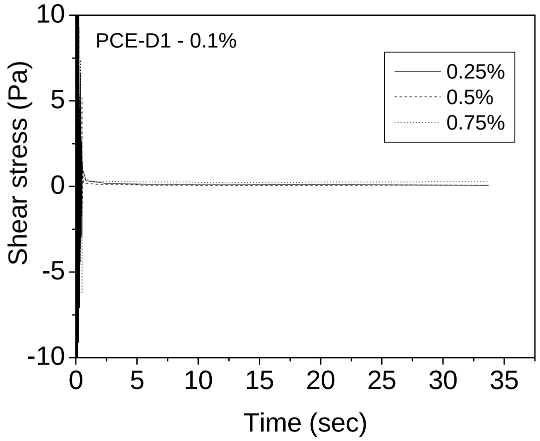
Tests were performed with different dosages of PCE-D1. It is seen that the shear stress decrease with increase in dosage of PCE based superplasticizer, as in Figure C.11 (a-e). Even though the paste shows stress relaxation at low dosages of 0.01% and 0.025%, the behaviour is viscous at higher dosages.



(a) Stress relaxation of PCE-D1, 0.01% (b) Stress relaxation of PCE-D1, 0.025%



(c) Stress relaxation of PCE-D1, 0.025% (d) Stress relaxation of PCE-D1, 0.07%

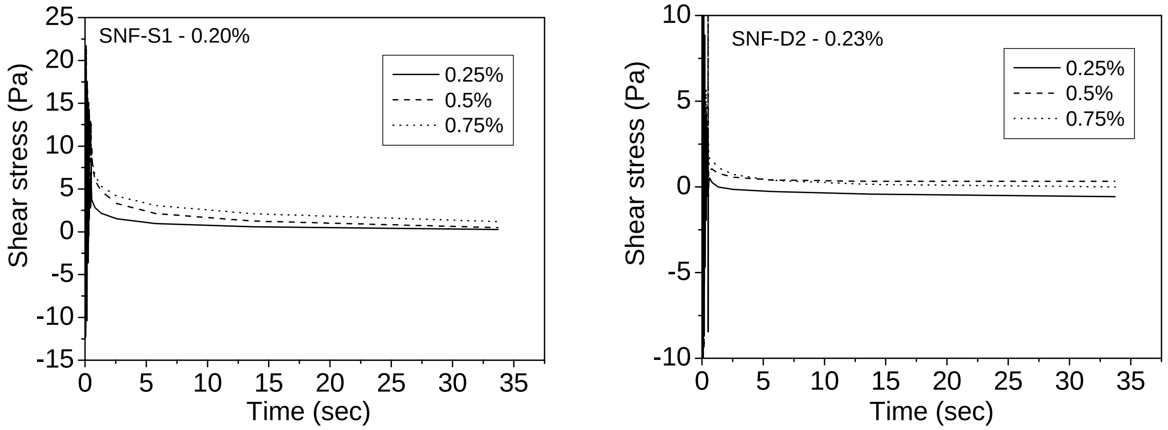


(e) Stress relaxation of PCE-D1, 0.1%

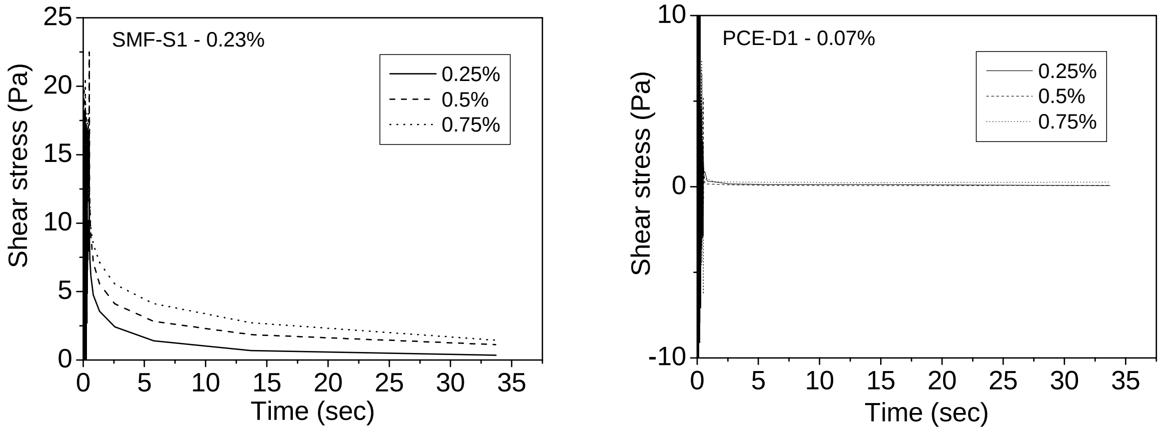
Fig. C.11 (a-e) Stress relaxation at different dosages of PCE-D1

Influence of saturation dosage of superplasticizer on stress relaxation

It is clear that the dosage of the superplasticizer affects the relaxation. From the tests on pastes with PCE-D1, it appears that at dosages much lower than the saturation dosages, there is appreciable relaxation with time whereas the behaviour is viscous at dosages higher than saturation dosages. At the saturation dosage, the paste with PCE-D1 has a practically viscous response. The stress relaxation shown by SNF-S1 and SMF-S1 at saturation dosage is appreciable but small whereas there is zero stress relaxation for the paste with SNF-D2 as in the case of PCE-D1 as shown in Figure C.12 (a-d). This results further confirms the viscous nature of superplasticized pastes at and beyond saturation dosages.



(a) SNF-S1, at saturation dosage (b) SNF-D2, at saturation dosage



(c) SMF-S1, at saturation dosage (d) PCE-D1, at saturation dosage

Fig. C.12 (a-d) Stress relaxation of pastes at saturation dosage of superplasticizers

C.5 Comparison of rheological tests

The creep and recovery and stress relaxation tests shows that a transition from non-linear viscoelastic to viscous nature occurs for pastes as the superplasticizer dosage changes from low to saturation and beyond. The saturation dosages obtained from Marsh cone tests are shown to yield viscous behaviour in all cases studied.

C.6. SUMMARY

In this investigation, steady shear, creep and recovery, and stress relaxation experiments were conducted on cement pastes with different superplasticizers of varying dosage rates. This helps develop an understanding of the transition of these mixtures from viscoelastic fluid-like materials to non-Newtonian fluids to linearly viscous fluids, as the superplasticizer dosage rate is increased. The work also increases the understanding of shear thinning characteristics as a function of superplasticizer type and dosage rates. The area of hysteresis cycles and shear thinning index were used for characterizing the shear thinning nature. As superplasticizer dosage increases, in general, there is a transition in the behaviour from viscoelastic to linearly viscous fluid behaviour. In the creep and recovery experiment, this is reflected as a linear change of strain with zero recovery during unloading. In the case of stress relaxation, the classical stress spike with zero stress after application of constant strain was seen. The dosages at which the change occurs compares well with the saturation dosages determined using the Marsh cone.

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LIST OF PAPERS SUBMITTED ON THE BASIS OF THIS THESIS

I REFERRED JOURNALS

1. **C Jayasree and Ravindra Gettu** (2008) Experimental Study of the Flow Behaviour of Superplasticized Cement Paste. *Materials and Structures,* RILEM, 41, 1581-1593.
2. **C Jayasree and Ravindra Gettu**. Correlations between the Fresh and Hardened Properties of Superplasticized Paste, Mortar and Concrete, *Indian Concrete Journal* (Under review)

II PRESENTATIONS IN CONFERENCES

1. **C Jayasree and Ravindra Gettu** Influence of Mixing Method on the Fluidity of Superplasticized Cement Paste**.** *Proceedings of the Fifth Asian Symposium on Polymers in Concrete*, Chennai, India, 11-12 September 2006, 665-670.
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3. **C Jayasree and Ravindra Gettu**. Mix Design of Self Compacting Concrete with Viscosity Modifying admixtures, *International Conference on Innovative World of Concrete*, 11-14 December 2008, New Delhi, India.