Some Studies on Use of Microfine Additives in Cement Paste and Mortar

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CIVIL ENGINEERING

(Computer Aided Structural Analysis and Design)

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Declaration

This is to certify that

i) The thesis comprises my original work towards the degree of Master of Technology in Civil Engineering (Computer Aided Structural Analysis And Design) at Nirma University and has not been submitted elsewhere for a degree.

ii) Due acknowledgement has been made in the text to all other material used.

- Maulik M. Panseriya

Certificate

This is to certify that the Major Project entitled **"Some Studies on Use of Microfine Additives in Cement Paste and Mortar"** submitted by **Mr.Maulik M.Panseriya (Roll No: 12MCLC16)** towards the partial fulfillment of the requirements for the degree of Master of Technology (Civil Engineering) in the field of Computer Aided Structural Analysis and Design of Nirma University is the record of work carried out by him under our supervision and guidance.The work submitted has in our opinion reached a level required for being accepted for examination. The results embodied in this major project work to the best of our knowledge have not been submitted to any other University or Institution for award of any degree or diploma.

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Abstract

Concrete is the widely used human made material in our civilization and most of its own properties are controlled by its main component, cement paste. The important property of concrete after strength is its workability. The main measurement of workability, the slump test, is not always applicable; at the same slump value, two concretes may exhibit different workabilities. On the other hand, hundreds of tests were designed over the years to measure the workability of concrete. The question is how to select the proper test for the application at hand and how to interpret the results obtained to predict the performance of the concrete in the field in the fresh state. To address these questions, it is necessary first to define workability in terms of fundamental physical entities, as described in the science of rheology.

To see the importance of durability of structure and the escalation in replacement costs of structures and the growing emphasis on the life-cycle cost rather than the first cost are forcing engineers to pay serious attention to durability issues. Next,there is a realization that a close relation exists between durability of materials and ecology. Two types of durability test are conducted as per their importance in construction industries. One is rapid chloride permeability test and chloride migration test.

Experimental investigation comprises preliminary investigation to find the effect of salient parameter on rheology of cement paste. Total five types of parameters are selected such as specific surface, particle size distribution, types of mineral admixture, water to cement ratio and co-relation between empirical test and fundamental test. Result of these parameters are used for selecting the types of different micro-fines, dosage of w/c ratio, and types of test for rheological investigation of cement paste.

For further investigation of rheological properties of micro fines, total seven types of microfines are selected at three different level of replacements 5%, 7.5% and 10%

and w/c ratio are 0.45, 0.5, 0.55 and 0.6 respectively. Rheological properties like mini slump flow, yield stress, viscosity, zeta potential are investigated and compared with the different cement pastes. Also a co-relation between minislump flow diameter and yield stress is developed. For measurement of yield stress and viscosity of cement paste viskomat Nt rheometer is used and for mini slump flow diameter mini slump cone is used. Result have indicated that among the seven different cement pastes containing different micro-fines at various dosages and w/c ratio tested, the paste with containing classified Fly Ash (P-100) was found giving the superior results by reducing the yield stress and viscosity, on the other hand, the Undensified silica fume gave the worst result. The cement paste rheological data were also compared using simpler tests, such as mini slump test. The goal was to determine whether the simpler tests could be used to characterize the rheology of cement paste adequately. The conclusions are that mini slump test is reliable to co-relate slump flow with yield stress.

Rapid chloride permeability and chloride migration two types of test is conducted for durability study of microfines. For durability test mix proportion of mortar is kept as 1:3 and w/c ratio-0.4. The performance of RCPT test on cement mortar evaluate based on charged passed and penetrability class. For chloride migration test performance is evaluate based on penetration depth of chloride ion and co-efficient of migration. Result of durability study indicated that the RCPT test value and migration co-efficient value of, Undensified Silica fume mix shows very low value while Alccofine mix shows very high value of RCPT compared to control and mix with Fly Ash shows higher value of migration co-efficient. The co-relation between RCPT and chloride migration test shows co-relation factor around 0.88.

Classified Fly Ash (P-100) is the suitable material for improvement of rheological properties of concrete, hence the pumpability and Silicafume is the suitable material for improve the durability of cocncrete against chloride ion.

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- Maulik M. Panseriya
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Abbreviation, Notation and Nomenclature

OPC .... Ordinary Portland Cement

SF .... Silicafume

MK .... Metakaolin

UFFA .... Ultra Fine Fly Ash

PSD .... Particle Size Distribution

PD .... Particle Diameter

w/c .... Water-Cement ratio

HRWR .... High Range Water Reducer

COV .... Co-efficient of Variation

τ .... shear stress

τ_0 .... yield stress

μ .... plastic viscosity

γ .... shear strain rate (1/s)

LOI .... Loss of Ignition

IR .... Insoluble Residue

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Chapter 1

Introduction

1.1 General

Concrete is the widely used human made material in our civilization and most of its own properties are controlled by its main component, cement paste. The important property of concrete after strength is its workability. To attain the better quality concrete, not only the proper mix design is required but also the quality control with sufficient compaction during construction is necessary.

Determining workability and desired properties by testing concrete is not always an option. It is generally accepted that the basic property influencing the performance of fresh concrete in casting and compaction is its rheological behavior. In recent years, there has been greater demand for the workability (flow properties) of fresh concrete to be estimated from rheological properties instead of conducting the large numbers of trials.

To achieve the desired properties and workability of concrete, water and admixture are added. These materials mainly affect the rheology of paste fraction since aggregate in concrete can be assumed as inert materials suspended in paste matrix.

Therefore, it is possible that the changes in the rheology of paste affect the rheology of concrete. Understanding the rheological behavior of paste fraction is essential to model accurately the workability of concrete combining with the physical effect such as size, shape and surface area of aggregate. Characterizing the rheological behavior of paste fraction will provide a means to improve concrete quality and optimize selection of parameters to produce better quality at lower cost.[1]

Next, durability of concrete is important for a variety of reasons,there is a general awareness now that designers of structures must evaluate the durability characteristics of the construction materials under consideration as carefully as other aspects, such as mechanical properties and initial cost. The escalation in replacement costs of structures and the growing emphasis on the life-cycle cost rather than the first cost are forcing engineers to pay serious attention to durability issues. Next,there is a realization that a close relation exists between durability of materials and ecology [2].

Main cause of deterioration of concrete structure is corrosion of steel reinforcement. The reason of corrosion of steel reinforcement mainly due to the carbon dioxide and especially chlorides are the main causes of damage. The rate at which chloride ions diffuse through concrete is a major determinant of the durability of structures. If chloride ions reach the vicinity of the rebar, the passive film around the steel can start to break down and the process of corrosion begins. The classical approach for ion transport in solutions states that if there is a difference in the concentration of ions in different regions, this gradient produces a flow of ions. Such a movement is called diffusion. In the same way, if there is a difference of electrical potential, this flow is called migration or electro-migration.

The principle of electro-migration tests is to apply a constant potential difference across a fully saturated sample. Usually they are performed in two chamber cells with the concrete or mortar in the middle, and each cell full of a defined solution. As the chloride is the ion of interest and the pore solution of concrete contains sodium, potassium and hydroxyls, these species are the most commonly used to fill the cells.[3]

1.2 Concrete Rheology

Freshly mixed concrete can be considered a concentrated suspension of aggregates in cement paste and can be measured as a viscous or viscoelastic fluid. Measurements of fluid rheology are typically based on the relationship between shear stress (τ) and shear rate (γ)expressed in a flow curve, as plotted in Fig.1.1. Typical rheological behavior indicated in a flow curve can be fit to a constitutive model. Concrete flow properties are most commonly characterized based on the Bingham constitutive model, which describes concrete flow in terms of yield stress (τ_0) and plastic viscosity (μ), as indicated in Eq.1.1. [4]

$$\tau = \tau_0 + \mu\gamma \tag{1.1}$$

Where,
τ = shear stress (Pa),
τ_0 = yield stress (Pa),
μ = plastic viscosity (Pa.s), and
γ = shear rate (1/s)

Yield stress represents the stress necessary to initiate or maintain flow whereas plastic viscosity expresses the increase in shear stress with increasing shear rate once the yield stress has been exceeded. Mixtures with high viscosity are often described qualitatively as being sticky or cohesive. Nearly all concrete exhibits a yield stress. Other models can also be used to represent concrete flow. In shear-thinning or shear-thickening power law fluids, the viscosity decreases or increases, respectively, with increasing shear rate.

The Herschel-Buckley model combines power law behavior with yield stress. Fluid rheology measurements are based on the representation of concrete as a fluid and are, therefore, most suitable for highly fluid concrete mixtures such as self-consolidating concrete. The use of the flow curves is inappropriate for very stiff concretes that exhibit more solid-like behavior, such as concrete with slump less than 50 mm (2 in.).

The flow models in Fig.1.1 represent steady-state behavior; however, rheological measurements are highly dependent on the shear history of a sample. This time dependence is due to thixotropy, which is defined as the reversible, time-dependent decrease in viscosity at a given shear rate. When a thixotropy material is at rest, a three-dimensional network structure develops over time due to factors such as colloidal forces.

The application of shear causes a breakdown of this network structure and a reorientation or deformation of particles or flocs, resulting in a reduction in viscosity at a constant shear rate or shear stress. After shear is applied for sufficient time, the material reaches an equilibrium condition where the viscosity is at a minimum for the given shear rate or shear stress. When the application of shear is stopped, the three-dimensional network structure reforms and the original viscosity are eventually restored. This time dependence must be taken into account when conducting rheological measurements. A structural model for the shear induced break down of cement systems are shown in Fig.1.2.

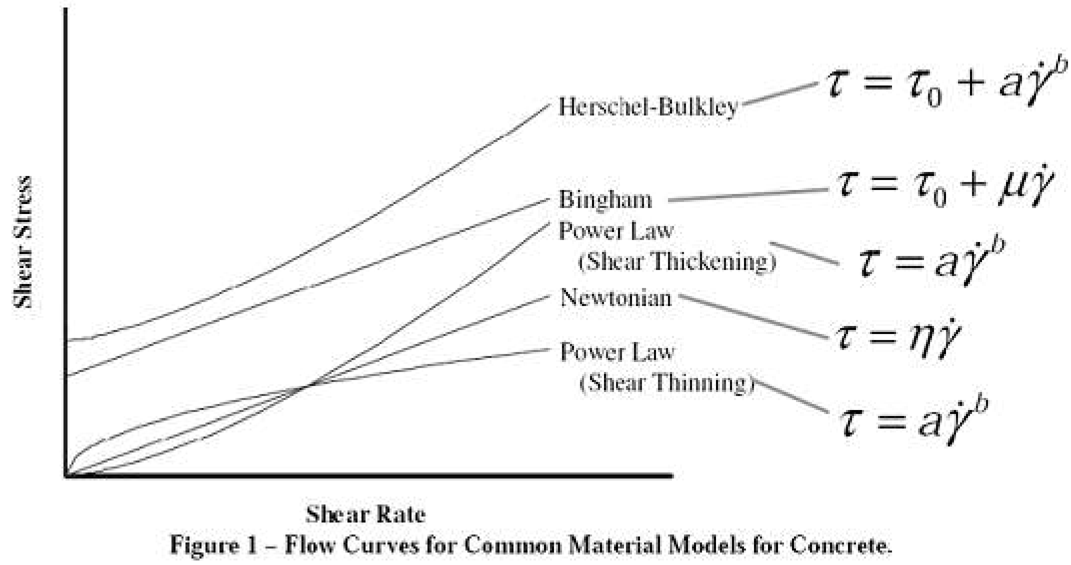

Figure 1.1: Flow curves for common material model for concrete

Due to thixotropy, concrete exhibits different flow behavior when at rest than when flowing. As discussed later, this distinction between at rest and flowing conditions is critical for concrete performance. In fact, yield stress can be more precisely distinguished as static yield stress and dynamic yield stress. Static yield stress is defined as the minimum stress to initiate flow from rest. Dynamic yield stress is the minimum stress to maintain flow after the breakdown of the thixotropy structure. Thus, four key rheological properties to measure are static yield stress, dynamic yield stress, plastic viscosity, and thixotropy.

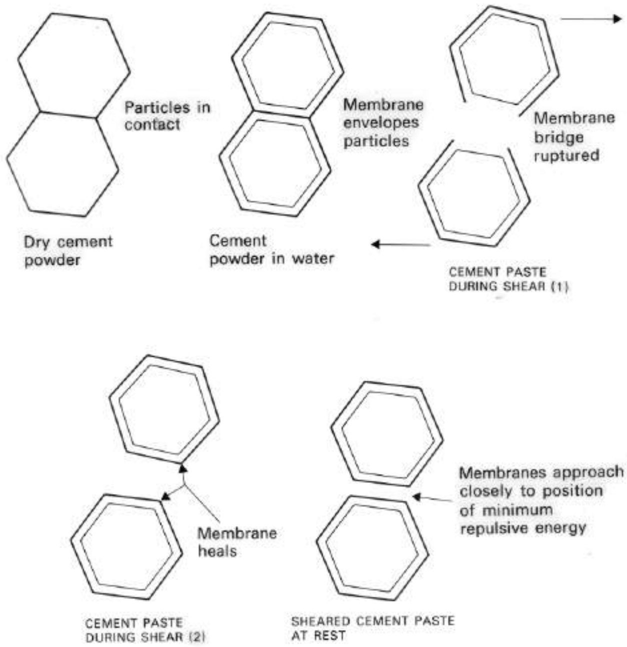

Figure 1.2: A structural model for the shear induced breakdown in cement systems.

Difference between Workability and Rheology

Workability: The ease, with which concrete can be mixed, placed, consolidated, and finished to a homogenous condition.

- Workability tests are typically empirical test.
- Tests simulate placement condition and measure value (such as distance or time) that is specific to the test method.
- Difficult to compare results from one test to another.
- Multiple tests needed to describe different aspects of workability.

Rheology: It is the study of the flow of matter, primarily in the liquid state, but also as 'soft solids' or solids under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force.

- Rheology provides a fundamental measurement of workability.
- Results can be used to describe multiple aspects or workability[5].

Factors affecting Rheology

The factors affecting paste rheology may be classified into two groups as internal and external factors. The internal factors are the composition of constituent materials in the paste itself and the external factors related to the environmental conditions, production method and testing conditions of the paste in conducting the tests for rheology. In the paste fraction, the internal control factors are not only the chemical but also the physical properties of the powder materials (cement and other inert powders).[6]

a. Internal Factors

- Chemical Factors
  - Interaction between different components
  - Properties of chemical admixtures
  - Chemical compositions of cement
  - Chemical reactivity of fine powder
- Physical Factors
  - Particle size and distribution of powders (cement and fillers)
  - Specific gravity
  - Geometrical shape
  - Surface texture

b. External Factors

- Temperature of the place where the paste is experiencing.
- Humidity or moisture content of surrounding area.
- Initial mixing conditions, such as mixing procedure, mixer speed.
- Shear history during conducting the test.
- Testing procedure such as test duration, measuring element.

Concrete Pumping Theory

Concrete flow prediction shall be based on the analysis of the concrete flow typology within a pumping pipe. This typology is complex but it is now accepted that flow of concrete in a pipe strongly differs from the one of typical viscous fluids such as water or oil.

The primary reason for this difference comes from the fact that concrete is a yield stress fluid (i.e. it flows only if the applied stress is higher than its yield stress). As a consequence, there exists at the center of the pipe (i.e. around the symmetry axis here the shear stress is equal to zero) a zone where concrete is not sheared.

Most approaches of concrete pumping in literature have taken into account this yield stress and the existence of this un sheared zone by assuming that concrete behaves as a Bingham fluid or Herschel Buckley fluid.

Concrete pumping is done by pushing concrete at high pressure into pipes made of either flexible, abrasion-resistant material or steel. The pressure applied provides the necessary thrust to move the concrete forward, i.e., it causes the concrete material to deform in the direction of the applied force and, hence, to transmit the force further. Indeed, the second reason for the difference between pumping of concrete and pumping of simpler materials comes from the fact that, under the action of shear, a redistribution of particles occurs within the pipe. This is a common feature of particle suspensions and initially well mixed particles in concentrated suspension flows are shown to undergo migration from high shear rate regions to low shear rate regions.

For example, in a Couette viscometer with a rotating inner cylinder and a stationary outer cylinder, the particles migrate towards the outer cylinder whereas in Poiseuille flows in cylindrical pipes, the particles migrate towards the central axis. This particle migration, in the case of coarse particles (i.e. particles with a characteristic size close to the characteristic size of the flow), can be increased by wall effect at the interface between the pumped material and the pipe.[7]

Indeed, because of simple geometrical considerations, it is not possible to find the center of a particle of diameter at a distance from a wall lower than a/2. During pumping, shear concentrates therefore in a fluid layer of material depleted from the coarsest particles of the concrete. In the inner region, the material is almost not sheared Fig.1.4. Pumping of concrete can therefore be considered in most cases as the shearing of an annular layer of unknown thickness and made of a material with unknown rheological properties.[8]

This layer is often called in literature lubrication layer or sometimes slippage layer, from a theoretical point of view, considering the rheological parameters of the material, pumping of concrete would not be possible without the formation of this lubrication layer. Sakuta et al.[8] went further and showed that the flow properties of the bulk material were irrelevant. The only property that matters is the ability of the material to form this layer. Rossig[9] pumped some colored concretes in a pipe for a direct observation of flow profiles. Their results demonstrated the existence of a high velocity and paste rich zone at the vicinity of the pipe wall.

Since coarse aggregates cannot be deformed easily, fresh mortar plays the major role in the deformation behavior of concrete. For most of the concretes it is evident from previous studies that concrete flows as a plug in the pumping pipelines, as illustrated in Fig.1.4; coarse aggregates move towards the center of pipe forming a core (plug), while an easily deformable, lubricating layer is formed at the internal walls of the pipelines, leading to a considerable reduction in the required pumping pressure. The lubricating mortar layer consists of cement paste (cement, water, mineral admixtures and chemical additives).[10]

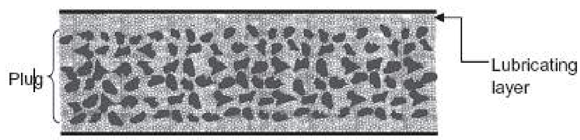

Figure 1.3: Schematic view of plug flow of concrete during pumping

1.3 Research Significance

Need of Rheological Study

Workability of Concrete is an essential component of concrete performance and has significant effect on economy, structural and durability properties of concrete. Rheology is the scientific measure of the workability of concrete. Modern concretes use more and more mineral admixtures to improve performance of material along with making the same more sustainable. Often Mineral admixtures like Fly Ash and Ground Granulated Blast Furnace Slags are used in large amount to replace normal Portland cements for improved structural and durability performance of concrete, where as Silica fume, Metakaolin, Microfine Slag, Fly Ash and fillers are used to improve one or another property of concrete. All these mineral admixtures alter the workability of concrete in different ways; some improves where as some makes the concrete viscous.

For determination of fresh property of concrete empirical test are widely used like slump test,V-funnel test, L-box test,compaction factor test etc. The main measurement of workability, the slump test, is not always applicable; at the same slump value, two concretes may exhibit different workabilities. On the other hand, hundreds of tests were designed over the years to measure the workability of concrete. The question is how to select the proper test for the application at hand and how to interpret the results obtained to predict the performance of the concrete in the field in the fresh state. To address these questions, it is necessary first to define workability in terms of fundamental physical entities, as described in the science of rheology. Slump test could reflect yield stress of concrete,which means rheological parameters could be used to evaluate pumping concrete.However, viscosity could be related to some of concrete workability which the slump test could not depict. So using rheology parameters to evaluate pumping concrete is reasonable.

Rheology plays an integral role in achieving the unique performance benefits associated with self consolidating concrete (SCC) and other high-performance concretes. These concretes will be pumped and rheology of concrete plays the main role in selection and design of concrete materials. The rheology will affect the economics of the pumping. Fluid rheology is a well established, widely used science that can be applied to the properties of fresh concrete. It is already known that proportion change influences concrete rheology, and workability is also changed. This is the base of relating workability to rheology. High-performance concrete (HPC) is a complex mixture often containing 5-10 different materials. Interaction between the various materials can cause wide variations in workability, which also depends on the specific materials and proportions used.

Admixtures mainly affect the flow behavior of the cement paste without altering the composition or behavior of the aggregates. It can be said that fresh concrete is a concentrated suspension of aggregates in cement paste and the cement paste itself is a concentrated suspension of cement grains in water. Therefore, it seems reasonable to try to select admixtures, chemical and mineral, by only testing the cement paste.

Need of Durability Studies

For durability properties, chloride ion is a serious issue for deterioration of structure. If chloride ions reach the vicinity of the rebar, the passive film around the steel can start to break down and the process of corrosion begins. So, the major determinant of the durability of structures is the rate at which chloride ion diffuse through concrete.

1.4 Objective of Study

To study various parameters, following objectives are decided for the major project.

Rheological study of micro-fine mineral admixtures

- To evaluate chemical oxides and physical properties of micro-fines such as particle size distribution, specific surface and compressive strength.
- To study the mini-slump flow behavior of micro-fines.
- To determined the rheological behavior of micro-fines in term of yield stress and viscosity.
- To examined the effect of water-cement ratio and dosages of micro-fines on rheology of cement paste.
- To study the co-relation between mini slump flow and yield stress.

Durability study of Microfine Additives

- To study the chloride penetration depth of cement mortar with different micro-fines.
- To calculate the chloride migration co-efficient of cement mortar with different micro-fines.

1.5 Scope of Study

In order to achieve objective of the study mentioned above, following scope of work is proposed. Scope of work is divided in two parts as follows.

a. Study the rheological behavior of micro-fines.

  - Collect and study the detailed information of different type of micro-fines such as Silica fume, Alccofine, Metakaoline, Fly Ash and Micro Talc.
  - Carry out preliminary analysis of micro-fine materials.
    - Chemical Analysis
    - Wet-Sieve analysis.
    - Specific Surface
    - Particle Size Distribution (PSD)
    - Compressive Strength
  - Decide the dosage of micro fine material and water for performing rheological test.
    - Dosage Of Micro fines
      - 5 %, 7.5 %, 10% replacement of cement by weight.
    - Dosages of Water
      - w/c ratio : 0.45, 0.5, 0.55, and 0.6

- Prepare the cement paste as per the dosage decided of micro fine with different dosages of water.
- Carry out Mini slump and viscometer test for cement paste rheology.
- Collect the data of slump flow from mini slump test, and collect the data of yield stress and viscosity from viscometer test.
- Investigate the influence of three variables (particle size distribution (PSD), different mineral admixtures, and water-cement ratio at each of the levels on the yield stress and viscosity of pastes.
- Co-relate the yield stress value with mini-slump flow diameter.

b. Study the durability properties of micro-fines.

- Prepare 1:3 mix-proportion of cement mortar with w/c-0.4 to investigate durability properties.
- Carry out Rapid chloride permeability test and chloride migration test.
- For RCPT duration of test is 6-hr after completion of test collect the data of charged passed and penetrability class from RCPT test.
- For chloride migration test duration of test is 24-hr after completion of test split the sample and spray the silver nitrate solution on one part of splited sample.
- Measure the depth of chloride penetration and carry out volhard titration for surface chloride concentration.
- Calculate the chloride migration co-efficient as per NT build-492.

Fig.1.4 shows the flow chart of experimental investigation to be conducted during the major project.

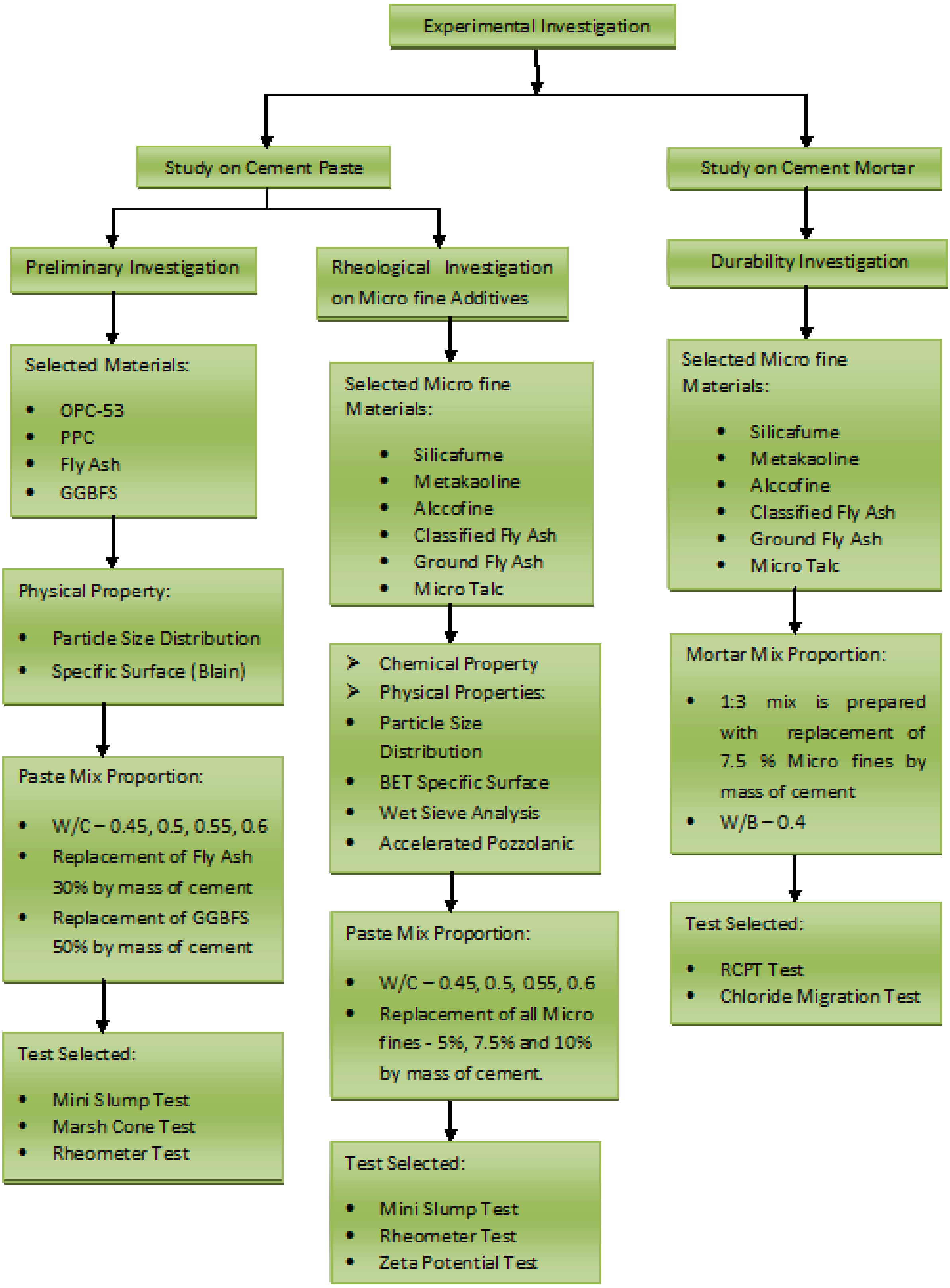

Figure 1.4: Flow chart of Experimental Investigation

1.6 Layout of Report

The report of major project is divided into seven chapters as given below.

Chapter 1 incorporates discussion about introduction and need of study of evaluate rheological and durability properties of concrete. Objectives of study and scope of work are further included in this chapter.

Chapter 2 includes the literature review based on previous research work related to the major project. It includes the concrete pumping theory, rheological measurement techniques, role of fine powder on rheology of cement paste,durability properties of mineral admixture mix concrete.

Chapter 3 describes the details of experimental programme. Material used in the investigation, mix proportion of cement paste for rheological investigation and cement mortar for durability investigation and the test procedure used are reported in this chapter.

Chapter 4 includes all results and discussion related to preliminary investigation of salient parameters affecting rheological performance of cement paste and reliability of rheological test.

Chapter 5 describes all results and discussion related to rheological properties including rheological parameter, mini slump flow diameter and co-relation between yield stress and mini slump flow diameter for different dosages of micro-fines and w/c ratio.

Chapter 6 describes all results and discussion of durability properties including rapid chloride permeability test, and chloride migration test of micro-fines mix cement mortar.

Summary, concluding remarks and possibility for future scope of work on basis of the work conducted in the major project has been incorporated in **Chapter 7**.

Chapter 2

Literature Survey

2.1 General

This chapter presents a brief review of the needs of different measurement techniques and effect of salient parameter on rheological and durability properties of cement paste or concrete. The past studies on rheology and durability of concrete or cement paste has been included in this chapter 2.

2.2 Rheological Measurement Techniques for Cement paste

As concrete construction applications become more demanding, there is increasing pressure on engineers to ensure high workability while at the same time maintain the structural properties necessary to meet design specifications.

For advancements to be made in understanding and controlling the workability of fresh concrete, testing procedures and industrial standards must move to a more fundamental quantitative basis. Accordingly, workability should be defined in terms of established measurable rheological parameters such as yield stress and viscosity. Several authors have acknowledged the need for a more quantitative measure of the fluidity of fresh concrete. However, measuring the fundamental rheological properties of concrete is experimentally challenging due to the large particle size of the aggregates. Furthermore, the equipment used for field testing must be relatively inexpensive, easy to use, and sufficiently small to be of practical use at construction sites. An attempt to utilize rheological measurements in cement paste as a reasonable indicator of concrete workability. Two types of rheological test:

- Empirical test
  - Mini slump Test
- Rheometer test

Rheological Measurement with Rheometer(Viskomat)

Flatt et al. [11] described the cement paste that was measured in the Viskomat contained 1 (w.r.t. cement) of a retarder solution.The water cement ratio was varied between the experiments and no super plasticizer was added. The objective of these experiments was to have pastes with varying yield stress and which would only undergo limited irreversible modification of this yield owing to ongoing hydration during the experiment. The water and retarder mixed together were added into the bowl already containing the cement. The total mixing time was 3 min. For the thickest pastes, the mixing was interrupted after 1 minute to homogenize manually the mix with a spatula (edges were not well mixed initially).
After the mixing was complete, the samples were again mixed by hand before placing into the Viskomat measuring pot (about 460 ml). All samples were then pre-sheared during 6 min at 160 min-1. This reduced substantially the torque, close enough to a plateau value to consider the sample had been well preconditioned and a steady state had been reached. The rotation frequency was then reduced at logarithmically spaced steps (160, 80, 40, 20, 10, 5 min-1), each step lasting 2 min. Flow curves were established with data corresponding to steady state only.

Comparison Between Empirical and Rheometer Test

Ferraris et al. [12] studied a fluid rheometer for cement paste is not widely available in the construction industry for many reasons. The two main reasons are:

- The instrument is relatively expensive and
- The importance of using such a device for cement paste was not advocated until recently.

Therefore, it would be advantageous to be able to use simpler tests such as the mini slump tests. A comparison between the rheometer and the mini slump test results is presented in Fig.2.1. Each point represents various mineral admixture additions at various dosages, w/c, and HRWR dosages. The plot of yield stress vs. mini slump spread diameter Fig.2.1 shows a weak correlation: Therefore, despite some of the scatter of the data shown on Fig. 2.1, an approximation of the yield stress could be obtained by fitting a straight line through the data. This fit will not be done here because it has a limited significance due to the wide scatter of the data.

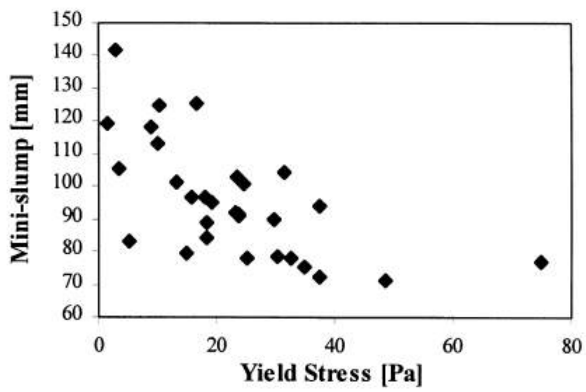

Figure 2.1: Comparison between rheometer and the mini slump test result

Reliability of Rheology Test

Hua et al. [13] studied that the reliability of the rheology test was evaluated by repeated tests. Three batches of concrete with one same mix design were prepared at the early state of research, the rheology test were performed on each of these mixes. The coefficients of variation (COV) of the yield stress and viscosity parameters were calculated respectively by dividing the standard deviation by mean. Results showed that the COV of the rheology parameters from the concrete rheology test are below 15%.

2.3 Effect of Fine Powders on Rheology of Cement Paste

Popovics [14] reported that, the addition of mineral admixtures improves concrete performance but reduces workability. The most common reason for poor workability is that the addition of a fine powder will increase the water demand due to the increase in surface area. However, in certain cases, it is reported in the literature that the use of fine mineral admixtures can reduce the water demand. The workability enhancement due to the use of certain fine mineral admixtures, especially Fly Ash (FA) or SF, is that the spherical particles easily roll over one another, reducing interparticle friction. It is a strong dependency of fluidity (defined as the inverse value of the viscosity). The spherical shape also minimizes the particle's surface to volume ratio, resulting in low fluid demands. Out of all 3D shapes, a sphere gives the minimum surface area for a given volume. A higher packing density was obtained with spherical particles as compared to crushed particles in a wet state. This resulted in lower water retention in the spherical case and subsequently lower water demand for a specific workability. A higher packing density was obtained with spherical particles as compared to crushed particles in a wet state. This resulted in lower water retention in the spherical case and subsequently lower water demand for a specific workability. From this survey of the literature that the selection of a fine mineral admixture for improved concrete workability is not a trivial problem. At present, this selection cannot be predicted from the physical or chemical characteristics of the admixture, and can only be determined using a properly designed test.

Effect of Different Types of Mineral Admixture on Flow Property of Cement paste

Ferraris et al. [12] showed that effect of mineral admixture type on cement paste rheological properties. In Fig. 2.2 the yield stress and viscosity are shown for mixtures composed of cement paste with the w/c ratio of 0.35 and varying dosages of HRWR.

The amounts of the various mineral admixtures by mass as replacement of cement are indicated on the figure. It is clear that the replacement of cement with UFFA leads to a decrease in the HRWR dosage over the control (no mineral admixtures) at a given yield stresses or viscosity.

In contrast, the replacement of cement by SF significantly increases the HRWR dosage at a given yield stress and viscosity. The addition of MK shows no significant improvement in yield stress and plastic viscosity over the control. Therefore, there are no significant rheological benefits or drawbacks in using MK as a mineral admixture, at least at the dosages tested.

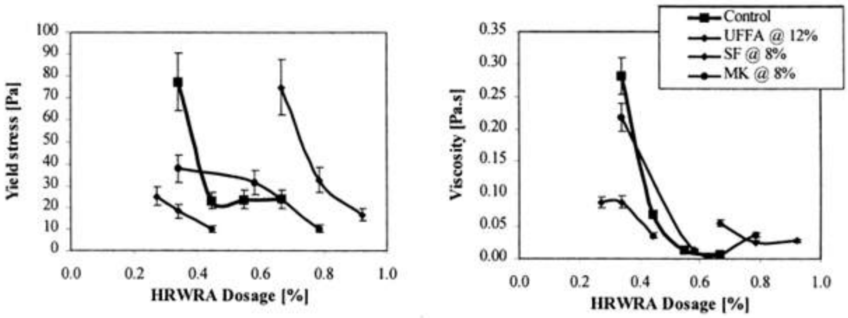

Figure 2.2: Dosage of HRWR and its effect on the flow of properties. The w/c ratio was 0.35.

Effect of Dosage of UFFA on Cement paste Rheological Properties

Ferraris et al. [12]studied that the influence of dosage of UFFA on cement paste rheological properties.The tests were done at a w/c ratio of 0.35 and a fixed HRWR dosage of 0.45 percent solid by mass of cement.The plot suggests that a dosage of 12 percent by mass is optimal for the best rheological properties. The dosage shows an optimum value corresponding to the lowest value achieved by the yield stress for a 12 percent UFFA by mass dosage.Fig.2.3

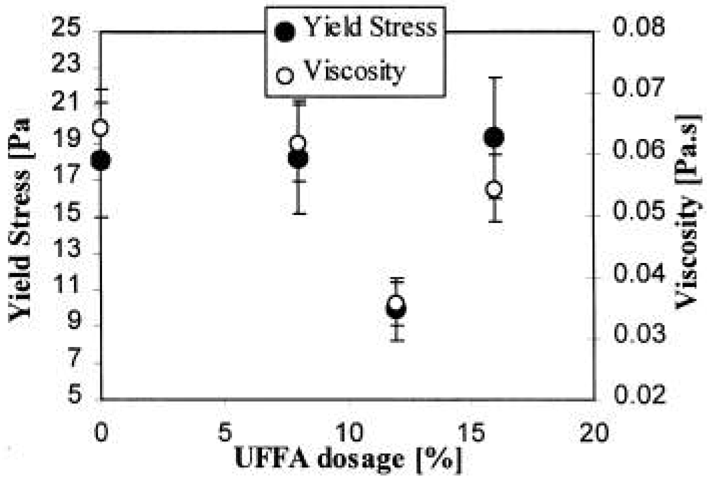

Figure 2.3: Dosage of UFFA and its effect on the rheological properties. The w/c ratio was 0.35.

Effect of PD on Cement paste Rheological Properties

Ferraris, et al. [12] showed that the rheological measurements for the four FA/cement pastes are plotted against the mean particle size of the FAs. Table 2.1 showed the particle diameter of different Fly Ash. All tests were conducted at the same dosage of mineral admixture (12percent replacement of cement by mass), same w/c ratio (0.35) and same dosage of HRWR (0.45percent solid by mass of cement). It is clear from the Fig.2.4 the lowest yield stress and viscosity are obtained at a mean PD of 3 μm. This value corresponds again to UFFA. It also seems that maximum viscosity is reached at a mean PD of about 11 μm, and maximum yield stress at a mean PD of 5.7 μm. This result seems to indicate an optimum and a pessimum PD, with the optimum at 3 μm and the pessimum at 5.7 μm.

Table 2.1: Particle Diameter of different Fly Ash

Sr.No	Name	PDμm,
1.	Coarse Fly Ash (CFA)	18.0
2.	Fly Ash (FA)	10.9
3.	Fine Fly Ash (FFA)	5.7
4.	Ultra Fine Fly Ash (UFFA)	3.1

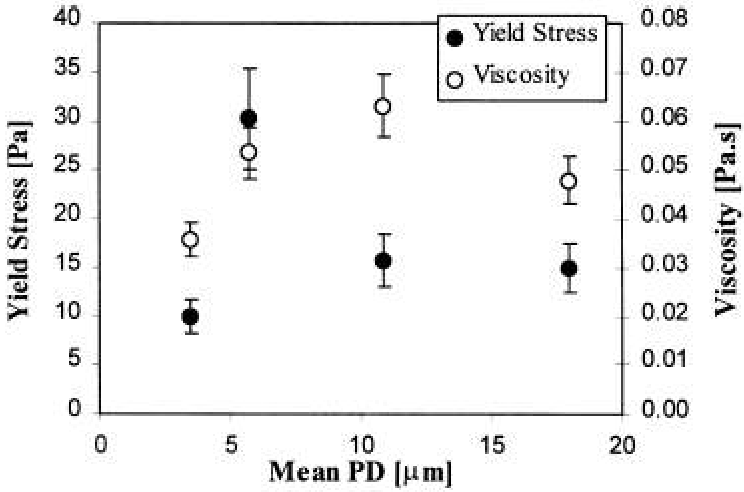

Figure 2.4: Influence of mean PD on the flow properties of cement paste.The w/c ratio was 0.35.

Effect of w/c on Rheological Properties of Cement paste

Ferraris et al. [12] shows that the results of tests performed on cement pastes with UFFA (at 12 percent replacement) at various w/c ratios, plotted vs. HRWR dosage. There are several ways to use or to interpret these results:

a. Determine the correct dosage of HRWR needed to obtain the same yield stress and/or viscosity with the UFFA mixes and the control at various w/c;

b. Determine the water reduction achieved by using UFFA and maintaining the same yield stress and/or viscosity;

c. Determine the reduction in HRWR dosage achieved while maintaining the same yield stress and/or viscosity.

In summary, the addition of UFFA improves the rheological properties.If the goal is to add UFFA and achieve the same yield stress and viscosity as the control,Fig.2.5 shows that the w/c ratio can be reduced by 10 percent and the HRWR dosage can be reduced by 40 percent. On the other hand, if the water content is reduced by 20 percent (w/c ratio of 0.28) a significant increase of the HRWR dosage (almost double) is needed to maintain the yield stress or viscosity, giving the same rheological behavior as the SF mixes.

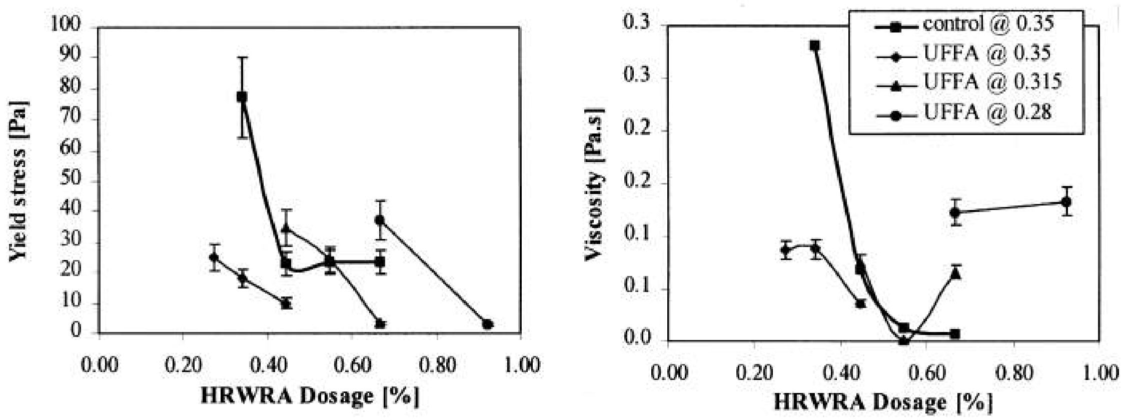

Figure 2.5: Influence of w/c ratio on the rheological properties of cement paste with UFFA at 12 percent replacement of cement by mass. The numbers in the legend indicate the w/c ratio used

Effect of Grinding of Fly Ash on Rheological Property of Cement paste

Grzeszczyk et al. [15] studied that the Portland cement produced in laboratory by grinding of Portland cement with gypsum (5 % by weight) to the specific surface of 328 m^2/kg and the high-calcium Fly Ash were used.

Raw fly ashes were used (FA-0) as well as the ashes preliminary ground for 7 min. (FA-1), 15 min. (FA-2) and 30 min.(FA-3).The specific surface areas of fly ashes are given in Table 2.2. The rheological investigations were prepared and homogenized in a laboratory mill within 5 hours.

The Fly Ash content in cement was 20, 40, 60 and 80 percent by wt of cement.The rheological measurements we carried out using the rotative viscometer type Rheotest RV-2.1, with the modified surfaces of both cylinders.All the cement-fly ash samples were prepared and measured following the same procedure and in the same conditions. The tests were performed at a constant temperature 21^{o}C and at constant water to solid ratio 0.5. Measurements started 10 minutes after mixing with water. The rheological properties of pastes with fly ashes were determined from the flow curves, at growing and reduced rates of shearing in the range from 0 to 146 s-1.
The yield value and plastic viscosity were determined from the descending part of flow curve, according to the Bingham's model and concluded A high-calcium fly ash admixture to cement results in a decrease in fluidity of pastes (higher yield value and plastic viscosity). Additional grinding of the high-calcium fly ash improves the rheological properties of pastes (increase in fluidity).

Table 2.2: Specific surface area of Fly Ash (Blaine)

Sr.No	Fly Ashes	Specific surface area of fly., ashes (Biaine) [m^2/kg]
1.	FA-0	261.9
2.	FA-1	393.2
3.	FA-2	430.2
4.	FA-3	471.3

Zeta Potential Theory

Colloidal systems having two (or more) separate phases: a dispersed phase and a continuous liquid phase. The dispersed particles are small, typically micron or smaller, called colloidal particles, many are nano particles. Slurry, paste, paint, toothpaste, milk, mayonnaise, emulsions, suspensions, etc.

Because their small sizes, colloidal particles have high specific surface area; consequently their surface characteristics, charge and morphology, and interfacial properties, play important roles in the stability and performances of colloidal systems. Zeta potential determination probes surface charge as well as surface morphology.

Particles in Liquid, when particles are dispersed in liquid, most of them will carry surface charge. The surface charge will attract ions of opposite charge to form a Stern layer where the ions are strongly bound and a diffuse region where they are less firmly associated. Fig 2.6 showed the different layer of colloidal particles in liquid.

It depends not only upon the particle surface but also on its environment. It can be affected by small changes in the pH or ionic strength of the medium. It also depends on surface morphology for "hairy" or even non smooth particles.[16]

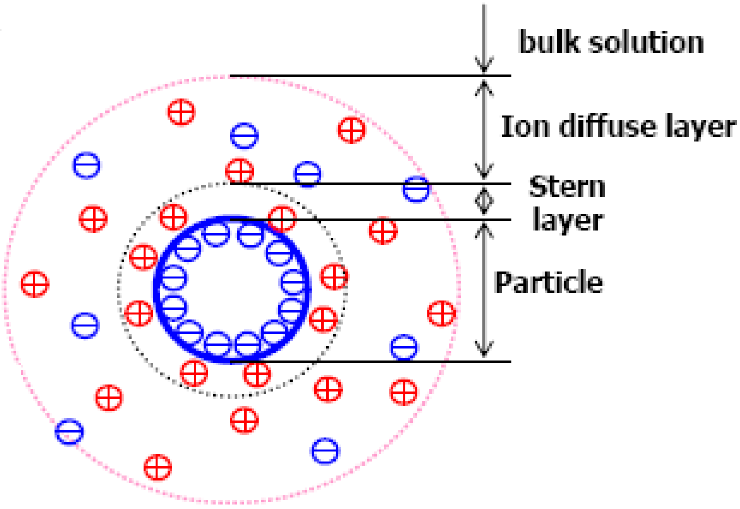

Figure 2.6: Colloidal Particles in Liquid

2.4 Durability Properties

General

The chloride-containing environment is conducive to the damage of reinforced concrete structures. The corrosion of reinforcement can start when the concentration of Cl^- ions at the steel surface reaches a critical value of about 0.4% by weight of cement contained in concrete. The diffusion coefficient of chlorides in the water-saturated concrete is usually measured by two methods. The first method is based on determining, at the fixed flow, the mass flux of chlorides and calculating the diffusion coefficient according to Fick's first law. In the second method, experimentally determined distribution of chloride concentration in concrete is compared with the result of the diffusion equation solved according to Fick's second law.

Both methods are long-lasting and provide the results for the ordinary concrete of a rather loose structure. However, conducting the tests on increasingly used high performance concrete in accordance with these rules is difficult because of its considerably higher tightness. That is why accelerated techniques based on forcing the flow of chloride ions through the electric field are undertaken.

The accelerated methods of chloride permeability in concrete employing the electric field were performed for the first time by Whiting. Later, they were adopted as a routine test in standards (AASHTO T277 and ASTM C1202). The tests on chloride diffusion coefficient based on their migration in the electric field were usually carried out in two chambers with electrodes. The chambers were separated by a thin specimen of concrete or mortar. The steady state mass flux, and then the value of apparent diffusion coefficient were determined while analyzing the concentration changes of chlorides penetrating the cathode chamber through the specimens.[17].

Role of Chloride ions in Iron Corrosion

Chloride ion actively destroys the protective film. If the protective oxide film is destroyed, the corrosion rate greatly increases. In general, chloride exists in three forms in cementitious materials.

Chloride can be chemically bound, being incorporated in the products of hydration of cement. Chloride ions react with $3CaO.Al_2O_3$ to form calcium chloroaluminate, $3CaO.Al_2O_3.CaCl_2 10H_2O$. A similar reaction with $4CaO.Al_2O_3Fe_2O_3$ results in calcium chloroferrite, $3CaO.Fe_2O_3.CaCl_2 10H_2O$. Chloride can also be physically bound, that is, adsorbed on the surface of the gel pores. Chloride can also be in the pore solution. The percentage of bound and free chloride greatly depends on the mortar composition and conditions of curing. Only free chloride can migrate.

The peculiar action of chloride ion is not completely understood. Some believe that, when the chloride ion concentration becomes large enough, ferrous chloride, or a ferrous chloride complex, is formed on the steel surface, replacing the protective oxide film. In the absence of the protective film, iron tends to turn into its thermodynamically more stable state, oxide or hydroxide, through a corrosion process. If the concentration of sodium chloride in cement is 1 % (w/w), then a typical corrosion rate may be 5.2 x 10^{-4} inch/year (for a cementitious material with a water to cement ratio of 0.42 (w/w)).

However, it is difficult to establish a universal corrosion threshold because in a specific concrete, the threshold depends on several factors, including the pH value of concrete, the water content, the proportion of water-soluble chloride, and the temperature.[18].

Theoretical Background of Chloride Migration Test

Lizarazo et al. [3] The migration Nordtest NT492 has been used extensively to find the non-steady-state migration coefficient. The analysis in it is based on the Nernst-Planck equation for a chloride mono-ion system assuming a semi-infinite homogeneous medium. If there is a chemical potential or concentration gradient and an electrical field, the flux for ionic transport can be expressed as 2.1.

$$J = D\frac{\partial c}{\partial x} - \frac{zF}{RT}DC\frac{\partial E}{\partial X} \tag{2.1}$$

where, D is the diffusion coefficient of species, z is the electrical charge, F is the Faraday constant [9.65 x104 Coulomb/mol], R is the gas constant [8.31 J/mol/K], T the absolute temperature [K], E the electrical voltage [V], C is the ionic concentration of the species in the pore fluid [mol/m^3], and x is the distance from the surface of the sample [m].

As electro-migration tests are carried out in laboratory facilities and the time is therefore limited to a few hours or days; the NT-Build 492 assumes that the diffusion term of the Nernst-Planck equation does not provide an important contribution to the total flux and can be considered to be negligible.
Thus:

$$J_M = \frac{z_i F}{RT} - D_i C(X,t)\frac{\partial E}{\partial X} \tag{2.2}$$

The mathematical solution for the Nernst-Planck equation 2.2 can be obtained using the error function

$$C(x,t) = \frac{C_s}{2}[e^{aX} ercf\frac{X + aDt}{2\sqrt{Dt}} + ercf\frac{X - aDt}{2\sqrt{Dt}}] \tag{2.3}$$

(where ercf is the complementary error function, C_s is the constant chloride concentration at the surface, and a is a constant related with the external voltage applied, defined by equation2.4.

$$a = \frac{zF\varphi}{RT} \tag{2.4}$$

In order to find the non-steady-state migration coefficient, the standard follows the recommendations of Tang and Nilsson [19]. It uses the mathematical solution for the Nernst-Planck equation for a chloride mono-ion system assuming a semi-infinite homogeneous medium. The equations given by the standard are summarized below.

$$D_{nssm} = \frac{RT}{zFE}\frac{X_d - \alpha X_d}{t} \tag{2.5}$$

$$E_f = \frac{U - 2}{L} \tag{2.6}$$

$$\alpha = 2\sqrt{\frac{RT}{zFE}} erf^{-1}(1 - \frac{2C_d}{C_0}) \tag{2.7}$$

Where, D_{nssm} is the non-steady state migration coefficient, [m^2/s], U the absolute value of the applied voltage [V], T the average value of the initial and final temperatures in the anolyte solution [K], L the thickness of the specimen [m], X_d the average value of the penetration depths [m], t the test duration [S], erf^{-1} the inverse of error function, C_d the chloride concentration at which the color of the silver nitrate indicator changes, C_0 the chloride concentration in the catholyte solution and E_f the electric field applied [V/m].[3]

Effect of Mineral Admixture on Chloride Permeability

Obla et al. [20] The RCPT test gives a rapid indication of the concrete's resistance to the penetration of chloride ions. Concrete specimens were tested at 28 and 91 days and 1 and 2 years. Results are presented in Fig 2.7.

It is clear that presence of UFFA has a very beneficial effect on the chloride permeability of concrete with significant reduction in the charge passed being observed as the level of UFFA increase. At 28 days, the RCPT test value of concretes with 8 to 16% UFFA are higher than those recorded for SF concrete of the same w/c. After 91 days, however, generally similar results are observed for all the concrete with either UFFA or SF. In fact the lowest RCPT value was observed for the mixture with 16% UFFA.

Concrete containing UFFA exhibited further reduction in the RCPT value between 91 days and 1 year. Between 1 and 2 years, however small increases were found in the charge passed for the mixtures containing UFFA. Similar trends were observed for the concrete containing SF, although the magnitude of the increase was much greater. In fact, the charge passed for the concrete with 8% SF has been increasing since the measurement was made at 28 days. The value at 2 years is 572 Coulombs compared with 393 Coulombs at 28 days; this represents an increase of almost 50% in the chloride permeability.

The concrete with 12% SF showed a 29% increase during the same period. While the difference in the RCPT values may be within the experiment error of the test, the consistent increase with time for both mixtures and the fact that a similar trend has been observed in a separate study, indicates that the general trend of increasing electrical conductance is a real phenomenon.

This may result, however from a change in the ionic concentration of the pore solution rather than a change in pore structure. It is also reported significant increases with time in the alkali concentration of the pore solution of pastes containing SF. In spite of the increase in RCPT value the concrete still satisfies a very low chloride permeability level, according to ASTM 1202.[20].

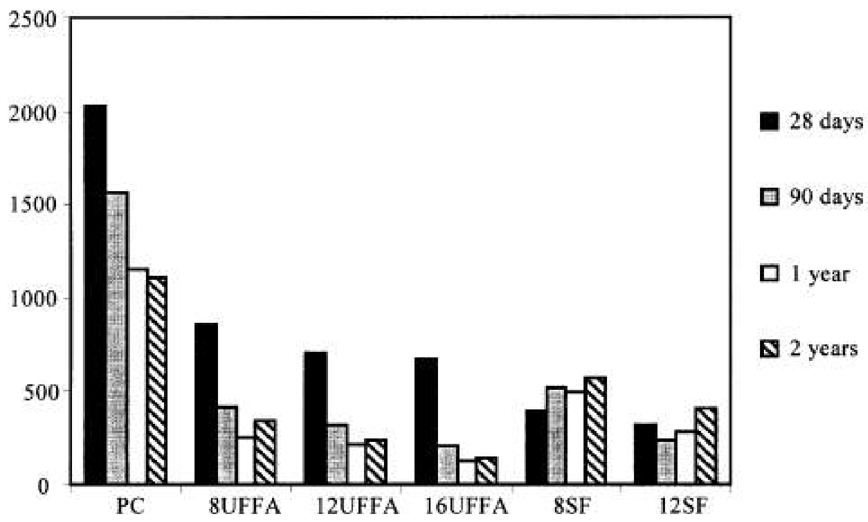

Figure 2.7: RCPT test results of different mineral admixture with different time period

Chapter 3

Experimental Programme

3.1 General

This chapter describes the experimental work. In these, materials, mixture proportion, and method of testing, of the blended cement paste are adopted during the investigation. This is followed by description of types of mix used, test parameters, and test procedures.

3.2 Materials

The materials used during the present investigations are Classified Fly Ash, Metakaoline, Ground Fly Ash Silica fume, Alcco fine and Micro talc as mineral admixture.

3.2.1 Silica Fume

Very fine pozzolanic material composed mostly of amorphous silica produced by electric arc furnaces as a byproduct of the production of elemental silicon or ferro-silicon alloys [21][22].

- Undensified Silica fume: Silica fume taken directly from the collection filter. The bulk density typically being in the range of 150-350 kg/m^3. Chemical properties of Undensified Silica fume are listed in Table 3.1. Fig 3.1 shows the Undensified Silica fume.

Table 3.1: Chemical Properties of Undensified Silica fume

Chemical Properties	Unit	Value
LOI	%	0.29
IR	%	79.86
SiO_2	%	93.96
Al_2O_3	%	0.42
Fe_2O_3	%	0.17
SO_3	%	0.66
CaO	%	0.36
MgO	%	0.59
Equivalent alkali (as Na_2O)	%	1.63

Figure 3.1: Undensified Silica fume

- Densified Silica fume: Silica fume that has been treated to increase the bulk density by particle agglomeration. The bulk density typically being above 500 kg/m^3. Chemical Properties of Densified Silica fume are listed in Table3.2. Fig 3.2 shows the Densified Silica fume.

Table 3.2: Chemical Property of Densified Silica fume

Chemical Properties	Unit	Value
LOI	%	2.40
IR	%	79.45
SiO_2	%	94.64
Al_2O_3	%	0.38
Fe_2O_3	%	0.24
SO_3	%	0.38
CaO	%	0.24
MgO	%	0.53
Equivalent alkali (as Na_2O)	%	0.38

Figure 3.2: Densified Silica fume

3.2.2 Fly Ash

Fly ash, the most widely used supplementary cementitious material in concrete, is a byproduct of the combustion of pulverized coal in electric power generating plants. In the process, the fused material cools and solidifies into spherical glassy particles called fly ash. The fly ash is then collected from the exhaust gases by electrostatic precipitator or bag filters. The specific surface area of Fly Ash can be increased in two ways.

- Classified Fly Ash: This type of Fly Ash is produced air classification process. However this process does not destroy the spherical shape of the fly ash.Chemical properties of classified Fly Ash is listed in Table 3.3. Fig 3.3 shows the SEM image of classified Fly Ash.

Table 3.3: Chemical Properties of Classified Fly Ash

Chemical Properties	Unit	Value
LOI	%	0.58
IR	%	92.93
SiO_2	%	55.94
Al_2O_3	%	32.17
Fe_2O_3	%	4.89
SO_3	%	0.23
CaO	%	1.38
MgO	%	0.73
Equivalent alkali (as Na_2O)	%	3.31

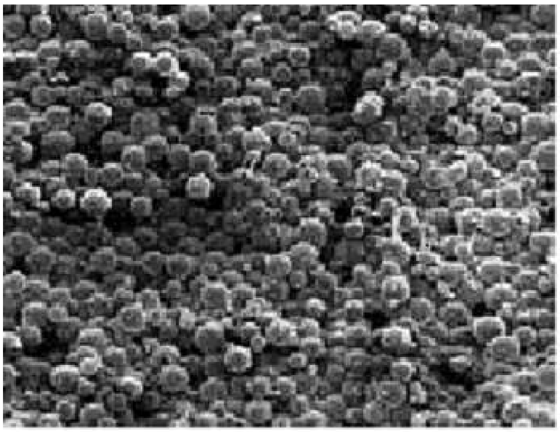

Figure 3.3: SEM image of Classsified Fly Ash

- Ground Fly Ash: This type of Fly Ash produced by mechanical processing or grinding. However, grinding breaks the sphericity of ash particles. Chemical properties of ground Fly Ash is listed in Table 3.4. Fig 3.4 shows the SEM image of Ground Fly Ash.

Table 3.4: Chemical Properties of Ground Fly Ash

Chemical Properties	Unit	Value
LOI	%	1.09
IR	%	93.95
SiO_2	%	59.11
Al_2O_3	%	30.53
Fe_2O_3	%	3.45
SO_3	%	0.23
CaO	%	1.41
MgO	%	0.51
Equivalent alkali (as Na_2O)	%	3.09

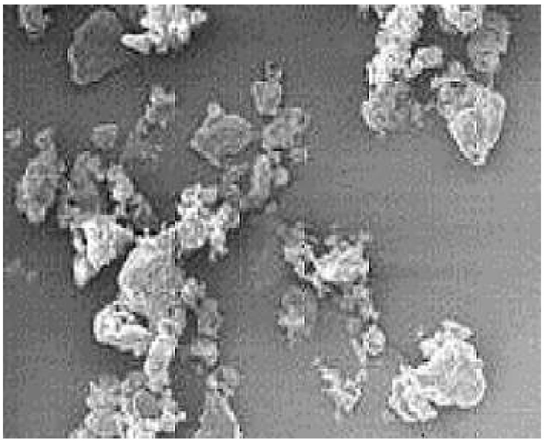

Figure 3.4: SEM of Ground Fly Ash

3.2.3 Alccofine 1203:

ALCCOFINE 1203 is a specially processed product based on slag of high glass content with high reactivity obtained through the process of controlled granulation. The raw materials are composed primary of low calcium silicates. It has distinct characteristics to enhance 'performance of concrete' in fresh and hardened stages. It can be considered and used as practical substitute for Silica Fume as per the results obtained.Chemical properties of Alccofine is listed in Table 3.5. Fig 3.5 shows the alccofine material.

Table 3.5: Chemical Properties of Alccofine-1203

Chemical Properties	Unit	Value
LOI	%	0.43
IR	%	0.79
SiO_2	%	33.28
Al_2O_3	%	21.24
Fe_2O_3	%	0.90
SO_3	%	0.22
CaO	%	34.01
MgO	%	5.79
Equivalent alkali (as Na_2O)	%	1.73

Figure 3.5: Alcco fine

3.2.4 Metakaolin (ASTM C-618)

Metakaolin, a special calcined clay, is produced by low temperature calcination of high purity kaolin clay. The product is ground to an average particle size of about 1 to 2 micrometers. Metakaolin is used in special applications where very low permeability or very high strength is required. In these applications, Metakaolin is used more. Metakaolin is in conformity with the general requirements of pozzolana classified by ASTM C 618 as Class N pozzolans[23].Chemical properties of metakaolin is listed in Table 3.6. Fig 3.6 shows the Metakaolin.

Table 3.6: Chemical Properties of Metakaolin

Chemical Properties	Unit	Value
LOI	%	2.35
IR	%	86.67
SiO_2	%	51.78
Al_2O_3	%	42.66
Fe_2O_3	%	0.55
SO_3	%	0.03
CaO	%	0.21
MgO	%	0.12
Equivalent alkali (as Na_2O)	%	1.18

Figure 3.6: Metakaolin

3.2.5 Micro Talc:

Micro Talc products are produced by Barrettes Minerals from an extensive deposit of high quality Montana talc (Magnesium Silicate) ore. Two general purpose grades are available: MICRO TALC 50-and, MICRO TALC 70-22 talc. These two products find application in sealants, joint compounds,texture coats, and other construction products. Chemical properties of Micro talc is listed in Table 3.7. Fig 3.7 shows the Micro Talc..

Table 3.7: Chemical Properties of Micro Talc

Chemical Properties	Unit	Value
LOI	%	43.18
IR	%	2.58
SiO_2	%	1.66
Al_2O_3	%	0.65
Fe_2O_3	%	0.16
SO_3	%	Nill
CaO	%	48.34
MgO	%	5.07
Equivalent alkali (as Na_2O)	%	0.48

Figure 3.7: Micro Talc

3.3 Physical Property

3.3.1 Wet Sieving

Separate determinations shall be made for the percentage of material passing 45-micron IS Sieve by wet sieving. Place 100 g of the material over each of the two sieves. Wash the material with a jet of water and keep it well agitated. The washing shall continue till the washings appear no more turbid. Dry the sieve and the residue in an oven. Brush the residue from the sieve after drying, and weigh on a balance sensitive to 0.1 percent of the weight of' the test sample. The percentage of material passing each sieve on wet sieving shall be reported to the nearest 0.1 percent by weight of the test sample. Allowable percentage retained on 45-micron sieve is 10 percent. Table 3.8 shows the result of wet-sieve analysis.

Table 3.8: Wet sieving of different micro-fines

Sr.No	Name	Percentage Retained on 45μm sieve
1.	Silica fume Undensified	0.7
2.	Silica fume Densified	6.46
3.	Metakolin	0.12
4.	Alcco Fine	0.04
5.	Classified Fly Ash (P-100)	0.14
6.	Ground Fly Ash	0.48
7.	Micro Talc	0.02

3.3.2 Particle Size Distribution

Particle Size distribution test is conducted on laser particle size analyzer. Range of particle size analyzer is between 0.04 micro-meters to 2500 micro meter.

3.3.2.1 Working Principle:

Laser diffraction analysis is a scientific technique which utilizes properties of the diffraction patterns of a laser beam passed through a substance, to measure the size of its particles. Laser diffraction analysis is based on the theory of Fraunhofer diffraction, which states that the intensity and angle of the light scattered by a particle is directly proportional to the size of the particle. The substance being examined is passed through the laser, and the diffracted light focused onto a detector which measures the angular distribution of the intensity of the scattered light. Fig 3.8 shows the laser particle size analyzer.

Figure 3.8: Particle size analyzer

3.3.2.2 Result of Particle Size Distribution

Particle size distribution of different micro-fines are performed by a laser diffraction techniques on a particle size analyzer. Results of diameters of particles at 10 percent passing (d_{10}),diameters of particles at 50 percent passing (d_{50}),diameters of particles at 90 percent passing (d_{90}) and mean diameters of particles are presented in Table 3.9.

Table 3.9: Particle Diameter of different micro-fines

Sr.No	Name	d10μm	d50μm	d90μm	Mean diaμm
1.	OPC-53	3.86	20.41	55.04	25.75
2.	Silica fume Undensified	2.03	6.3	12.39	6.85
3.	Silica fume Densifeid	3.13	11.75	26.97	13.63
4.	Metakaolin	1.41	5.74	20.25	8.55
5.	Alcco Fine	1.18	3.56	8.33	4.24
6.	Classified Fly Ash(P-100)	1.27	3.68	9.61	4.65
7.	Ground Fly Ash	1.67	7.16	21.05	9.45
8.	Micro Talc	1.02	3.42	10.02	4.61

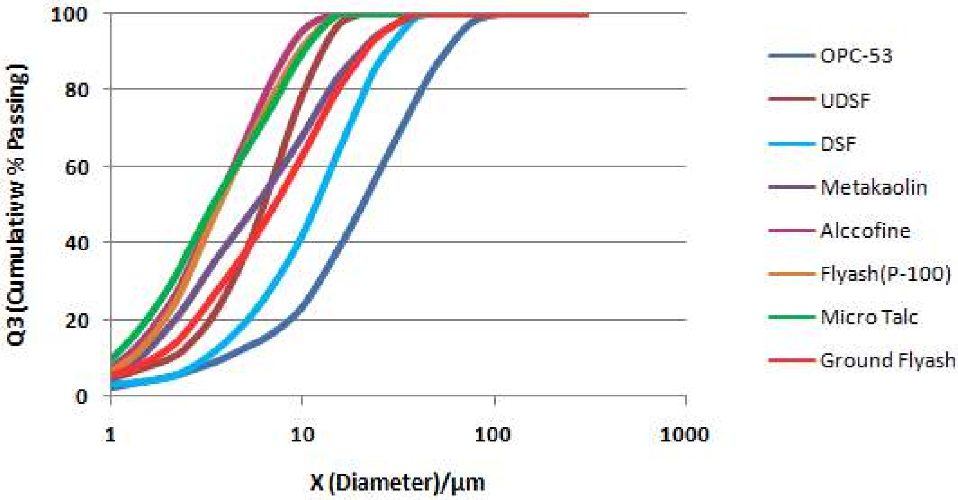

Figure 3.9: Particle Size Distribution of Micro fines material

3.3.3 Specific Surface

Specific Surface of the micro-fine materials conducted on BET- analyzer.This method of test specifies the determination of the total specific external and internal surface area of disperse or porous solids by measuring the amount of physically adsorbed gas according to the method of Brunauer, Emmett and Teller (BET method).The BET method cannot reliably be applied to solids which absorb the measuring gas.

3.3.3.1 Working Principle:

The method specified involves the determination of the amount of adsorbate or adsorptive gas required to cover the external and the accessible internal pore surfaces of a solid with a complete monolayer of adsorbate. This monolayer capacity can be calculated from the adsorption isotherm using the BET equation. Nitrogen at its boiling point (about 77 K) is usually the most suitable adsorptive.

The monolayer capacity n_m is calculated using the BET equation.

$$\frac{\frac{p}{p_0}}{n_a[1-\frac{p}{p_0}]} = \frac{1}{n_m C} + \frac{C-1}{n_m C}.\frac{p}{p_0} \tag{3.1}$$

Where, p = pressure of the adsorptive in equilibrium with the adsorbate, Pa

p_0 = saturation vapour pressure of the adsorptive, Pa

n = specific amount adsorbed, mol g^{-1}

n_m = specific monolayer capacity of adsorbate amount of adsorbate needed to cover the surface with a complete monolayer of molecules

C = BET parameter.

3.3.3.2 Result of Specific Surface Area

Specific surface area of different micro-fines are determined by a gas adsorption using the BET method. Results of specific surface ares of micro-fines are presented in Table3.10.

Table 3.10: Specific Surface of different micro-fines

Sr.No	Name	Specific surface Area (m^2/gm)
1.	OPC-53	0.280
2.	Silica fume Undensified	18.153
3.	Silica fume Densifeid	20.282
4.	Metakaolin	10.466
5.	Alcco Fine	2.191
6.	Classified Fly Ash(P-100)	1.303
7.	Ground Fly Ash	1.301
8.	Micro Talc	3.692

3.3.4 Accelerated Pozzolanic Strength Activity Index

Accelerated pozzolanic strength activity index is performed by testing 50mm × 50mm cement mortar cube. Mix proportion of control mix and test mix according to ASTM

C-1240 is given below.

Control Mix:

- 500 g of portland cement
- 1375 g of graded standard sand, and
- 242 mL of water.

Test Mix:

- 500 g of portland cement
- 1375 g of graded standard sand, and
- 242 mL of water.
- X grams of dry high-range water reducer (Type F), required to produce a flow of 100 to 115 %.

For the mixing of mortar digital mortar mixture is used. First add the high-range water reducer directly to the mixing water in the mixing bowl. Then add the cement or the cement-Micro-fines mixture and start the mixing cycle. Mixing procedure is according to ASTM C-305.

Mixing Procedure:

- Select the cycle speed first 60-sec 140 rpm.
- Next 30 sec 285 rpm.
- Stop the mixture for 90 sec.
- Quickly scrape down for any paste that may have collected on the side of the bowl.
- Finish by mixing 1 min at 285 rpm.

Figure 3.10: Digital Mortar Mixture

3.3.4.1 Flow table Test

Flow table test was performed according to ASTM C-1437 to check the necessary flow of mortar can be produce or not. Procedure of flow table test is describe below. Mix proportion for flow table test is same as used for in accelerated pozzolanic strength activity index.

Test Procedure:

- Place the flow mold at the center.
- Place a layer of mortar about 25 mm in thickness in the mold and tamp 20 times with the tamper.
- The tamping pressure shall be just sufficient to ensure uniform filling of the

mold.

- Then fill the mold with mortar and tamp as specified for the first layer.
- Wipe the table top clean and dry.
- Lift the mold away from the mortar 1min after completing the mixing operation.
- Immediately drop the table 25 times in 15 s.

Figure 3.11: Flow table test apparatus

3.3.4.2 Compression Test

The compressive strength of mortar has been evaluated on a 1000 kN capacity hydraulic testing machine. For the compressive strength test, cubes of size 50mm $\times$ 50mm $\times$ 50mm are tested in compression in accordance with the test procedures given in ASTM C-109. Equation of finding out compressive strength of the cube specimens is given below.

$$Compressive strength = \frac{P \times 10^3}{A} \tag{3.2}$$

Where, P = Failure load of cube (kN)

A = Area of cube (50 × 50) (mm^2)

Figure 3.12: 50mm × 50mm × 50mm cube mould

3.3.4.3 Result of Accelerated Pozzolanic Strength Index

Accelerated pozzolanic strength activity index of micro-fines are determined by performing compression test on 50 mm × 50 mm cube at 7-days. Result of accelerated pozzolanic strength activity index and flow of mortar of all micro-fines is given in below Table3.11.

Table 3.11: Accelerated pozzolanic strength activity index of micro-fines

Name	Dosage of SP (dry) (%)	Flow (%)	7-days Compressive Strength(MPa)	Accelerated Pozzolanic strength index
OPC-53	Nill	105	21.47	1.00
Undensified Silica fume	0.48	105	28.53	1.33
Densified Silica fume	0.42	100	22.75	1.06
Metakaolin	0.44	112.5	27.93	1.30
Alcco Fine	Nill	101.4	26.83	1.25
Classified Fly Ash (P-100)	Nill	117.5	20.6	0.96
Ground Fly Ash	Nill	110.4	21.23	0.99
Micro Talc	Nill	113	20.86	0.97

3.4 Rheological Properties of Cement Paste

3.4.1 Mix-proportion for Rheological Investigation

As rapid construction demand, concrete is pumped by pumping truck and its requiring higher workability in terms of fluidity or pumpability. The workability enhancement due to the use of certain fine mineral admixtures, especially fly ash (FA) or Slag, is that the spherical particles easily roll over one another, reducing interparticle friction.It is a strong dependency of fluidity.

It is also noted that use of this micro-fines materials is also enhance the concrete structural and durability performance. Dosage of these micro-fines materials and w/c ratio is selected based on the Indian standard for different exposure condition, cement content maximum free water cement ratio and standard grade of concrete ranges (M-25 to M-55).

- Dosage of micro-fines: 5%, 7.5% and 10% of the replacement of cement by mass.
- w/c ratio: 0.45, 0.5, 0.55, and 0.6.

3.4.2 Mini Slump Test

3.4.2.1 General

The mini-slump, which was originally, developed by Kantro (1980) to measures the consistency of cement paste. The mini-slump cone is simply a small version of the slump cone. The mini-slump cone has a bottom diameter of 38 mm, a top diameter of 19 mm, and a height of 57 mm. The cone is placed in the centre of a glass plate on which the diagonals and medians are traced.[10]

Figure 3.13: Mini Slump

3.4.2.2 Mini Slump Test Procedure

Mini slump test is empirical test for measuring the slump flow diameter of cement paste. Test procedure of mini slump test is presented here.
100 gm cement sample has been taken and mix with water for different w/c ratio. Poured slurry of cement paste in to cone. The cone is lifted and after one minute, the average spread of the paste, as measured along the two diagonals and two medians,

is recorded for different types of cement paste with different w/c ratio.[10]
Like the conventional slump test, the results of the mini-slump test should be related to yield stress so, draw the graph of flow diameter Vs yield stress measure with viscometer and shows correlation between them.

3.4.3 Rheometer Test

3.4.3.1 General

Viscometer or Rheometer is instrument used to characterize the rheological properties of materials, typically fluids that are melts or solution. These instruments impose a specific stress field or deformation to the fluid, and monitor the resultant deformation or stress. Instruments can be run in steady flow or oscillatory flow, in both shear and extension.
Rheometer is a laboratory device used to measure the way in which a liquid, suspension or slurry flows in response to applied forces. It is used for those fluids which cannot be defined by a single value of viscosity and therefore require more parameters to be set and measured than is the case for a viscometer. It measures the rheology of the fluid. It allows ramping from 0.001 rpm to 200 rpm in both directions to record flow curves and yield points. The torque up to +/-250 Nmm is measured by a measured by a special transducer.

Figure 3.14: Viskomat NT with modified cement paste probe

3.4.3.2 Rheometer Test Procedure

Rheometer is a laboratory device which is used for measuring the rheological parameter.Measuring Process are presented here.
500 gm of cement and water accordingly w/c ratio of 0.45, 0.5, 0.55, and 0.6 has been taken. Mix them thoroughly with mechanical mixture about 2 min. Pour it into the Viskomat vessel up to the marking ring and start the Viskomat for measurement. The following steps are involved in taking a Viskomat measurement.

- Defining the profile -Step or Ramp

- After defining the profile assigning a name for measurement file and start the Viskomat with start button

- After completion of measurement collecting the measured data and display graphical evaluation of the measured data.

Table 3.12: Input Profile - Step

Sr.No	times	Speed of Probe (RPM)
1.	5 min	120
2.	10 min	100
3.	15 min	80
4.	20 min	60
5.	25 min	40

- Due to the complicated flow pattern applied to the tested paste by the probe. It is difficult to obtain the exact value of shear stress and shear rate of the tested paste.

- Therefore, the torque and the speed of the probe were reported during the paste rheology tests and their relationship was plotted.

- The following equation was used to fit the down curve from a Viskomat rheology test based on Bingham model:

- For fit the Bingham model select the Approximation option. For represent a flow curve instead of the original measured data, select the corresponding flow curve model. For Bingham model select the option given in 3.3.

$$T = H * N + G \tag{3.3}$$

- Where T was the torque acting on the impeller, and N was the rotation speed of the impeller. G was the interception of the linear portion of a down curve and the y-axis. H was the slope of the linear portion of the down curve.

- Plot the data and collect the value of yield stress (G) and viscosity (H).

3.4.4 Zeta Potential Test

3.4.4.1 General

The action of plasticizer is mainly to fluidity the mix improves the workability of concrete, mortar or grout. The mechanisms that are involved could be explained in the following way:

Dispersion of Portland cement, being in fine state of division, will have tendency to flocculate in wet concrete. These flocculation entraps certain amount of water used in the mix and thereby all the water is not freely available to fluidify the mix.

When plasticizers are used they get adsorbed on the cement particles. The adsorption of charged polymer on the particles of cement creates particle to particle repulsive forces which overcome the attractive forces. This repulsive force is called Zeta Potential, which depends on the base, solid content, quantity of plasticizer used. The overall results are that the cement particles are deflocculated and dispersed. When cement particles are deflocculated, the water trapped inside the flocs get released and now available to fluidify the mix. Fig.3.15 explains the mechanism.

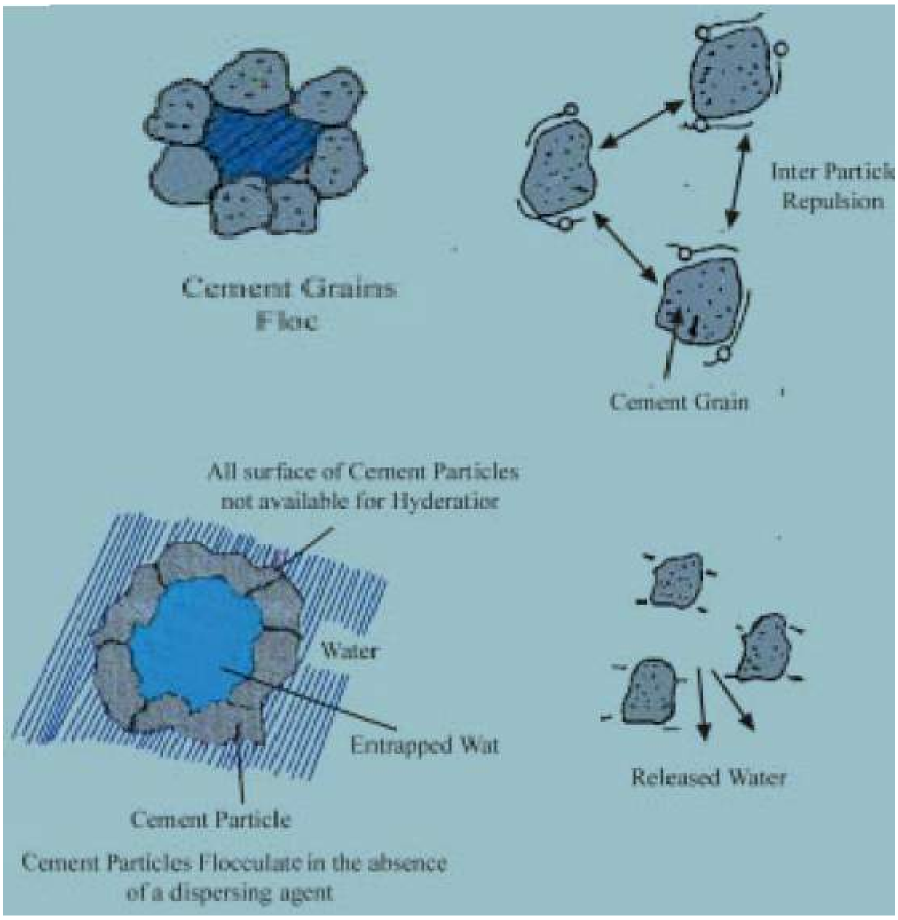

Figure 3.15: Mechanism of Zeta Potential

3.4.4.2 Zeta Potential Test Procedure

Zeta potential of any mix is measured by zeta potential analyzer. Zeta potential analyzer is worked on the principal of colloidal dynamics and measures the electrostatic repulsion in terms of mili volt (mV).

- Prepare Slurry of all micro fine additives with 7.89% solid concentration. (30 gm of micro fine mix with double distilled water.)
- Poured the slurry into the cup then insert the zeta probe, and pH probe mounted on the panel.
- Define the RPM of the stirrer which is mounted at bottom of the cup. Regulate the RPM through the regulator given at the panel.
- For all the micro-fines 200 RPM is kept for measure zeta potential.
- After setting the RPM, data logging is start on the screen in which enter the file name, test duration times, and delay times between measurements.
- Click the particle properties and enter the value of particle concentration, particle density ratio, and die-electric constant.
- Similarly enter the solvent properties (generally used water), solvent viscosity, solvent dielectric constant etc.
- After entering all the inputs start the measurement by clicking the measure tab.
- It will measure pH, conductivity, dynamic mobility and zeta potential.

Figure 3.16: Zeta Probe Analyzer

3.5 Durability Properties of Cement Mortar

In order to investigate durability properties of different micro-fines two types of durability test are selected in accordance with their importance in construction field.

- Rapid Chloride Permeability Test (RCPT).
- Chloride migration test.

3.5.1 Mix-Proportion

For chloride migration and RCPT test mix proportion for control mix and test mix are listed below.

Control Mix

- OPC-53 cement - 650 kg/m^3.
- Standard Sand - 1950 kg/m^3.

- Water - 260 kg/m^3.
- W/B - 0.4.

Test Mix

- OPC-53 cement - 601.25 kg/m^3.
- Micro-fines mineral admixtures - 48.75 kg/m^3 (7.5 % replacement of cement by mass)
- Standard Sand - 1950 kg/m^3.
- Water - 260 kg/m^3.
- W/B - 0.4.

3.5.2 Preconditioning

Before the RCPT and Chloride migration test started following preconditioning is to be applied to the specimen. After cutting the specimen, brush and wash away any burrs from the surfaces of the specimen, and wipe off excess water from the surfaces of the specimen. When the specimens are surface-dry, place them in the vacuum container for vacuum treatment. Both end surfaces must be exposed. Reduce the absolute pressure in the vacuum container to a pressure in the range of 10-50 mbar (1-5 kPa) or 50 mm Hg within a few minutes. Maintain the vacuum for three hours and then, with the vacuum pump still running, fill the container with distilled or de-ionized water then immerse all the specimens. Maintain the vacuum for a further hour before allowing air to re-enter the container. Keep the specimens in the solution for 18$\pm$2ours. Fig3.17 shows the preconditioning setup.

Figure 3.17: Desiccator and Vacuum Pump

3.5.3 Preparation of alkaline Solution

For chloride migration test two types of alkaline solution is required sodium chloride (NaCl) and sodium hydroxide (NaOH). Concentration of sodium chloride is kept approximately 10 % NaCl by mass in distilled water (100 g NaCl in 900 g water approximately 2N) for chloride migration test and for rapid chloride permeability test (RCPT) concentration of NaCl is kept 3% by mass in distilled water and concentration of sodium hydroxide is kept 0.3 N consisted of 0.3 x 40 = 12 grams of NaOH solids (in pallet form) per liter of the solution, where 40 is the molecular weight of NaOH for both the test.[24]

3.5.4 Rapid Chloride Permeability Test

This test method is based on the ASTM 1202. It requires cylindrical specimens of 100 mm diameter and a thickness of 50 mm. An external electrical potential (60 V) is applied across the sample. In RCPT test solution used for catholyte is 3% Nacl by mass in distilled water and for Anolyte 0.3 N NaOH solution is used. Read and record current at least every 30 min. Plot current (in amperes) versus times (in seconds). Draw a smooth curve through the data, and integrate the area underneath the curve in order to obtain the ampere-seconds, or coulombs, of charge passed during the 6-h test period. Fig3.19 shows the test setup of RCPT.[24]

3.5.5 Chloride Migration Test

This test method is based on the NT Build 492. It requires cylindrical specimens of 100 mm diameter and a thickness of 50 mm. An external electrical potential is (30 V) applied across the sample in order to force the chloride ions to migrate into specimen for 24-hr. After the test, the sample is split in to two parts and a silver nitrate solution sprayed on to one of the sections. The penetration depth is measured from the chloride precipitation. From the other axially split specimen, cut an approximately 5 mm thick slice parallel to the end surface that was exposed to the chloride solution. Determine the chloride content in the slice in accordance with NT BUILD 208 or by a similar method with the same or better accuracy and then migration coefficient can be calculated using equations given in the standard. The solutions used in the cathode and anode are a 10% NaCl and a 0.3 N NaOH respectively.Fig3.19 shows the chloride migration setup.[25]

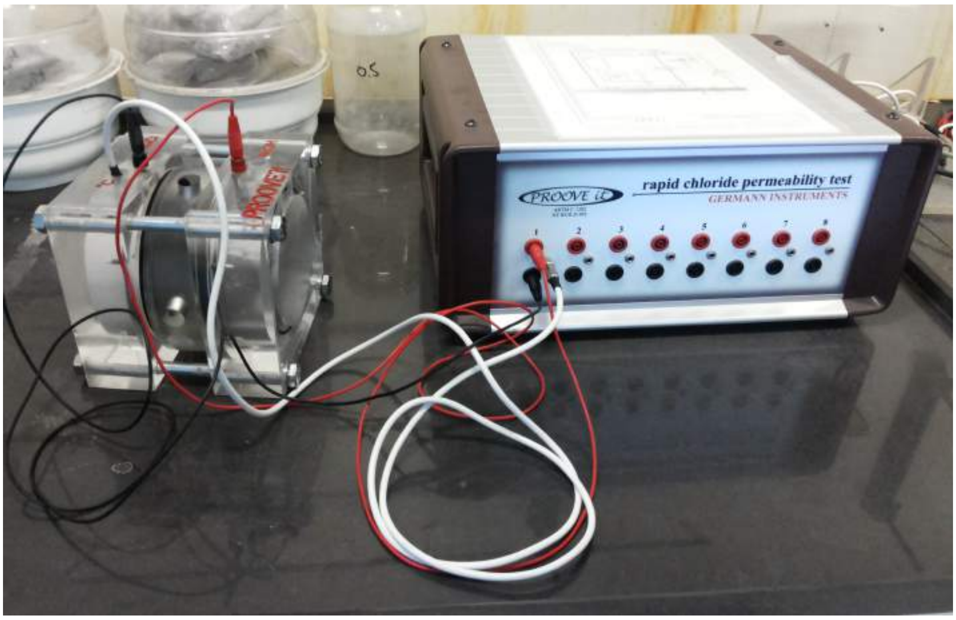

Figure 3.18: Rapid Chloride Permeability Test and Chloride Migration Test Setup

Figure 3.19: Cutting Machine and Cylindrical Mould

Chapter 4

Preliminary Investigation for Rheological Study of Cement Paste

4.1 General

In this chapter, the results of preliminary investigation are presented and discussed by means of tables and plots. Rheological properties for blended cement pastes based on these results is also described in detail.

Four parameter from the below list have been used in the preliminary investigation. Co-relation between minislump flow and yield stress and marsh cone flow time and viscosity has also been investigated.

a. Type of mineral admixture

b. w/c ratio

c. Particle Size Distribution

d. Specific Surface

For preliminary investigation four types of cement paste is used for investigate the rheological properties. Dosage of water to cement is kept as 0.45, 0.5, 0.55 and 0.6. Types of cement paste and replacement level of mineral admixture are listed below.

- OPC-53 cement paste.
- PPC cement paste.
- OPC + Fly Ash (30% replacement)cement paste.
- OPC + GGBFS (50 % replacement) cement paste.

4.2 Physical Properties

4.2.1 Particle Size Distribution

Particle size distribution of different mineral admixtures are performed by a laser diffraction techniques on a particle size analyzer are presented in Fig4.1.

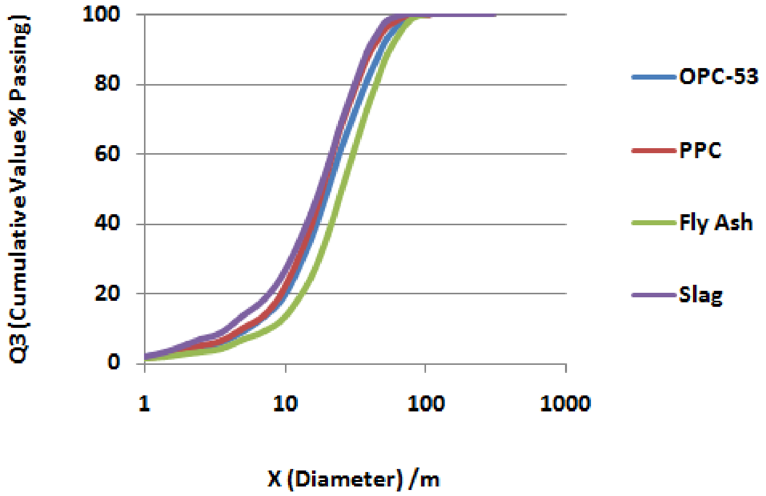

Figure 4.1: Particle Size Distribution of Mineral Admixtures

4.2.2 Specific Surface

Specific surface area of different mineral admixture are determined by blain apparatus are give in below Table 4.2.2.

Table 4.1: Specific Surface of different Mineral Admixtures

Sr.No	Name	Specific Surface Area (m^2/Kg)
1.	OPC-53	277
2.	PPC	355
3.	Fly Ash	298
4.	Slag	314

4.3 Effect of Mineral admixture on mini slumpflow of cement paste

In order to investigate effect of mineral admixture on minislump flow of cement paste. Four types of cement paste with four different w/c ratio is selected for investigation. From the Table4.3 shows that OPC + Fly Ash paste shows the higher value of minislump flow diameter compare to control (OPC-53 paste) while PPC paste shows the least diameter value.

Table 4.2: Mini slumpflow diameter (cm) of four different types of cement paste.

w/c ratio	**OPC-53**	**PPC**	**OPC + Flyash**	**OPC + Slag**
0.45	9.85	6.2	8.3	7.9
0.5	10.9	7.8	9.75	9.4
0.55	13.45	10.5	10.8	10.35
0.6	17.45	11.3	11.3	11.55

4.4 Effect of Mineral admixture on Marsh cone flow time of cement paste

In order to investigate effect of mineral admixture on marsh cone flow time of cement paste. Four types of cement paste with four different w/c ratio is selected for investigation. From the Table 4.4 its shows that OPC + Fly Ash paste takes longer time to flow to the control (OPC-53 paste).

Table 4.3: Marsh cone flow time (Sec) of four different types of cement paste.

w/c ratio	**OPC-53**	**PPC**	**OPC + Fly Ash**	**OPC + Slag**
0.45	462	-	-	-
0.5	62	379	607	952
0.55	37	58	100	54
0.6	14	52	62	39

4.5 Effect of Mineral admixture on Rheological parameter (Yield stress & Viscosity) of cement paste

In order to investigate rheological parameter of cement paste four different types of cement paste is selected and tested in Viskomat NT rheometer for measuring yield stress and viscosity. From the Fig 4.2 and Fig 4.3 its clearly shows that Portland pozzolana cement (PPC) shows the higher yield stress and viscosity compare to other mineral admixture namely Fly Ash and GGBFS to the control sample (OPC-53) while OPC + Fly Ash and OPC + GGBFS shows the least value.

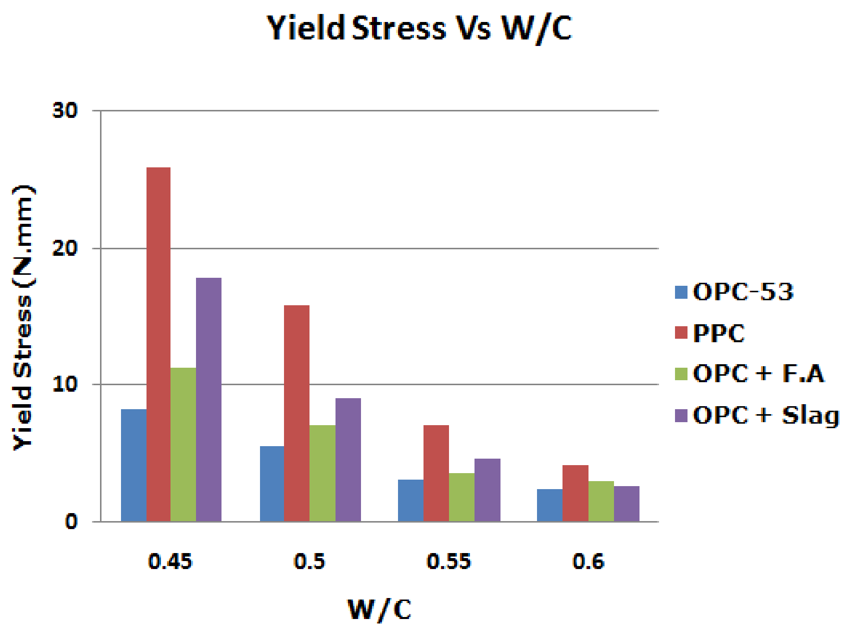

Figure 4.2: Effect of Mineral admixture on Yield Stress

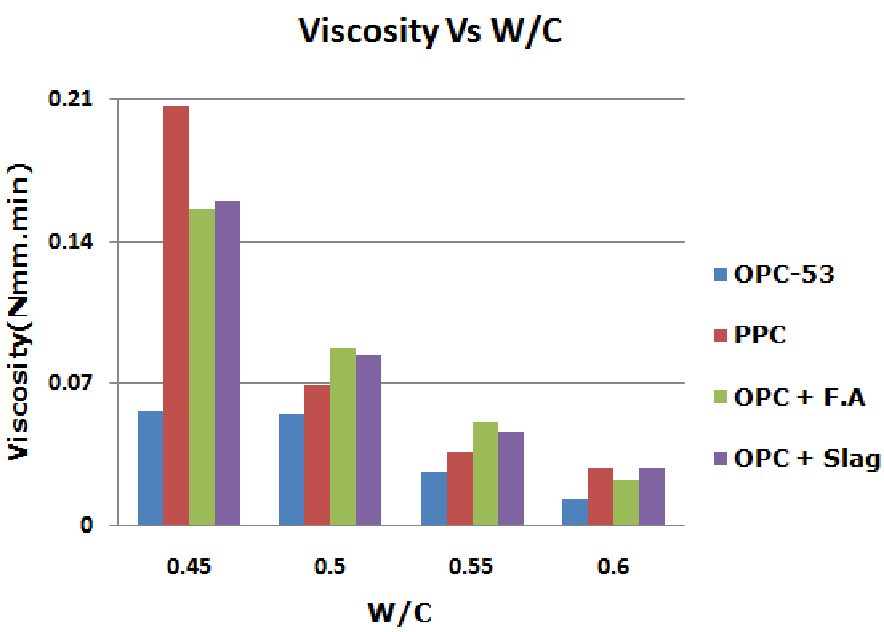

Figure 4.3: Effect of mineral admixture on Viscosity

4.6 Co-relation between Empirical test and Rheometer test

The main reasons for co-relate the rheometer data to less sophisticated test such as marshcone and minislump are: the instrument cost and the importance of using such a device for cement paste was not much popular.If relationship could be established, the empirical tests could be used to design materials for a given yield stress and viscosity.

The co-relation between marshcone flowtime and viscosity shows no co-relation while from the Fig 4.4 shows that co-relation between minislump flow diameter and yield stress shows good co-relation factor. So, It is conclude that co-relation between minislump flow diameter and yield stress is more useful and reliable.

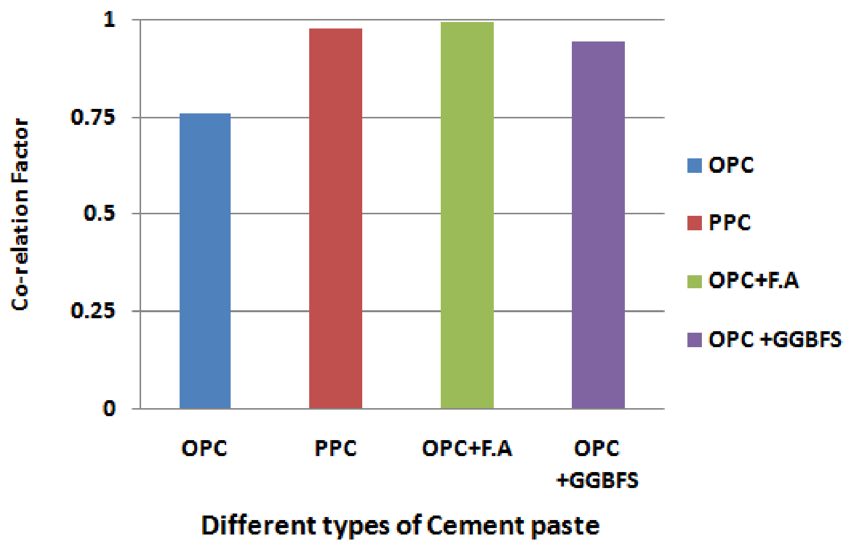

Figure 4.4: Co-relation between Minislump flow diameter and Yield stress for different cement paste

Chapter 5

Evaluation of Rheological Properties of Cement Paste

5.1 Mini Slump Test

Result of Mini slump flow diameter of various micro fines with different dosages and w/c ratio are presented in the Table 5.1 - 5.8.

Table 5.1: Slumpflow diameter of OPC-53

w/c ratio	Slumpflow diameter
0.45	9.16
0.5	11.35
0.55	13.45
0.6	17.85

Table 5.2: Slumpflow Diameter of Undensified Silica fume

w/c ratio	**Slump flow Diameter in (cm)**		
	5%	7.5%	10%
0.45	5.33	3.1	2.8
0.5	7.38	5.6	5.18
0.55	9.58	9.93	5.23
0.6	12.75	11.1	7.95

Table 5.3: Slumpflow Diameter of Densified Silica fume

w/c ratio	**Slump flow Diameter in (cm)**		
	5%	7.5%	10%
0.45	7.25	6.8	6.73
0.5	10.3	10.23	10.13
0.55	13.05	12.53	11.55
0.6	16.83	15.23	14.12

Table 5.4: Slumpflow Diameter of Metakolin

w/c ratio	**Slump flow Diameter in (cm)**		
	5%	7.5%	10%
0.45	6.53	5.21	3.93
0.5	8.013	7.063	6.39
0.55	8.29	7.46	7.94
0.6	12.74	10.08	10.063

Table 5.5: Slumpflow Diameter of Alcco-fine

w/c ratio	**Slump flow Diameter in (cm)**		
	5%	7.5%	10%
0.45	7.11	6.84	6.76
0.5	9.61	9.19	9.01
0.55	13.29	12.14	11.71
0.6	16.59	14.86	15.16

Table 5.6: Slumpflow Diameter of Classified Fly Ash (P-100)

w/c ratio	**Slump flow Diameter in (cm)**		
	5%	7.5%	10%
0.45	8.94	8.01	7.96
0.5	12.51	9.96	11.34
0.55	14.96	13.09	12.66
0.6	16.94	16.06	14.04

Table 5.7: Slumpflow Diameter of Ground Fly Ash

w/c ratio	**Slump flow Diameter in (cm)**		
	5%	7.5%	10%
0.45	7.36	8.24	9.64
0.5	12.01	11.81	12.59
0.55	14.01	15.91	14.98
0.6	16.31	15.94	14.78

Table 5.8: Slumpflow Diameter of Micro Talc

w/c ratio	**Slump flow Diameter in (cm)**		
	5%	7.5%	10%
0.45	8.54	8.31	7.41
0.5	11.93	11.56	11.49
0.55	14.96	12.64	14.54
0.6	16.61	16.01	16.39

5.1.1 Effect of Microfine Additives on Minislump Flow

In Fig.5.1 5.2 and 5.3, the slump flow are shown for different blended cement paste with the various w/c ratio of 0.45, 0.5, 0.55,and 0.6 and various dosage of micro-fines. The amounts of the various mineral admixtures by mass as replacement of cement are indicated on the top of figure. It is clear that the replacement of cement with Classified Fly Ash at dosage 5% gives a greater slumpflow at w/c-0.5 and 0.55 compare to control. While Ground Fly Ash and Micro Talc gives better performance at dosage of 7.5% replacement and w/c ratio 0.5 and 0.55 compare to control. Similar behavior is seen at dosage of 10% replacement. In contrast Undensified Silica fume gives poor performance compare to control mix.

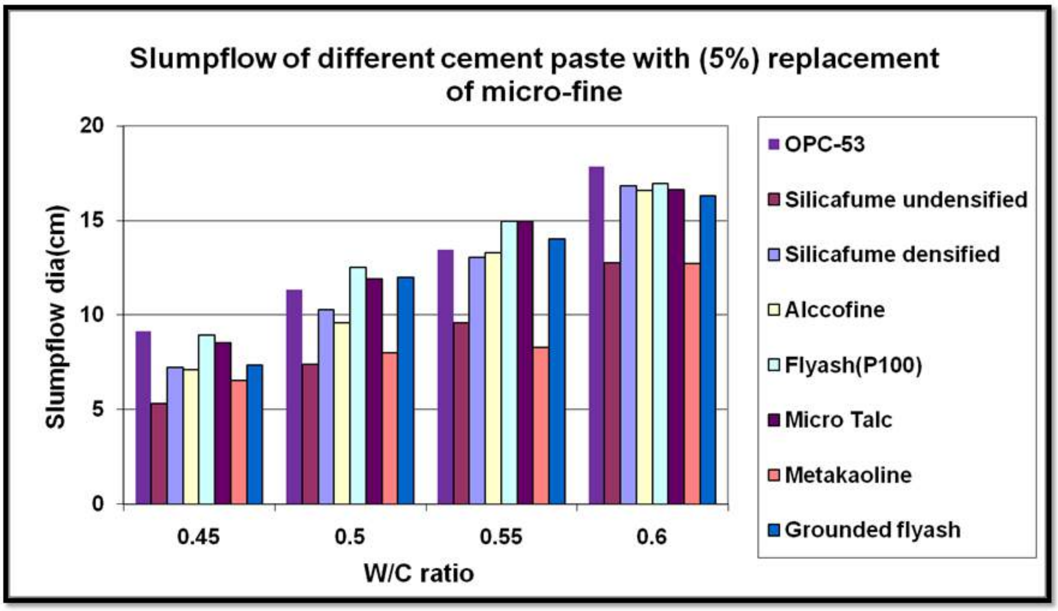

Figure 5.1: Effect of Micro-fines mineral admixture (5%) replacement on slumpflow

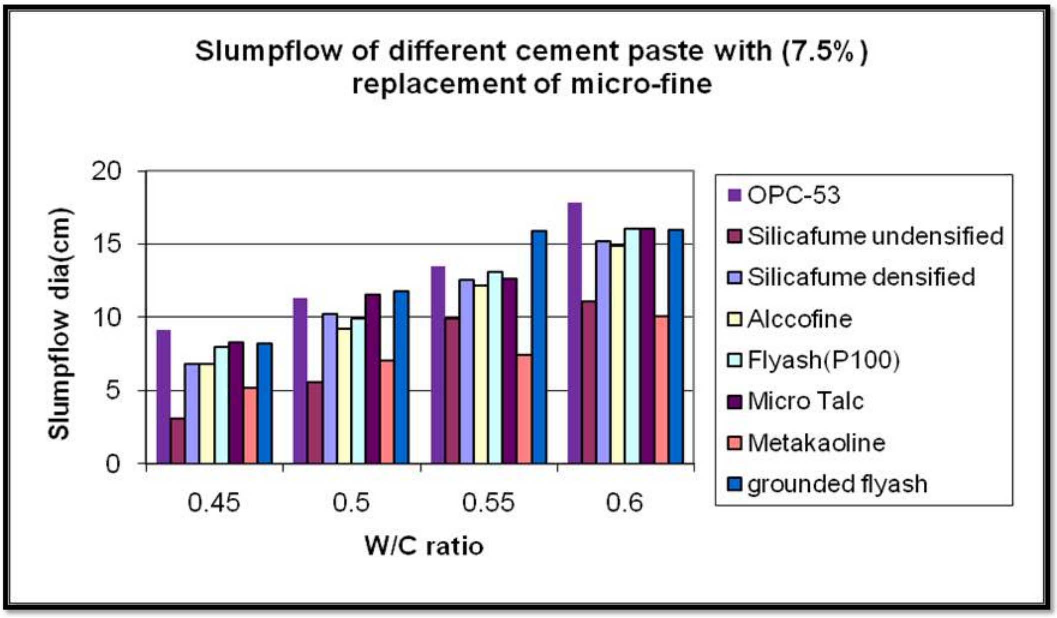

Figure 5.2: Effect of Micro-fines mineral admixture (7.5%) replacement on Slumpflow

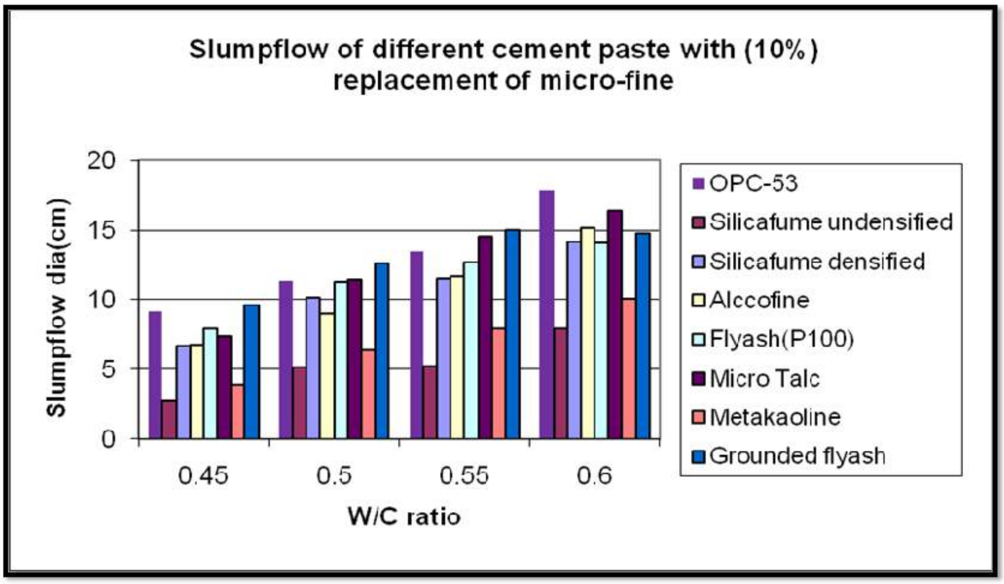

Figure 5.3: Effect of Micro-fines mineral admixture (10%) replacement on Slumpflow

5.2 Rheometer Test

This test is conducted to check the influence of micro-fine materials on Rheology of cement paste. This test is also conducted to measures rheological parameter namely yield stress and viscosity. This test is performing on Viskomat Nt rheometer for 25 mins. After 25 min plot the curve between Torque acting on probe and RPM refer Fig5.4; fit the straight line For Bingham model **T=H*N + G.** Collect the value of Yield stress from intercept and value of viscosity from slope of the straight line 5.5 Results of yield stress and viscosity of different paste is shown in Table.

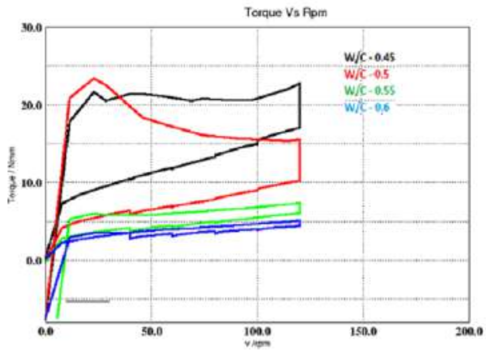

Figure 5.4: Original flow curve of cement paste with varying w/c ratio

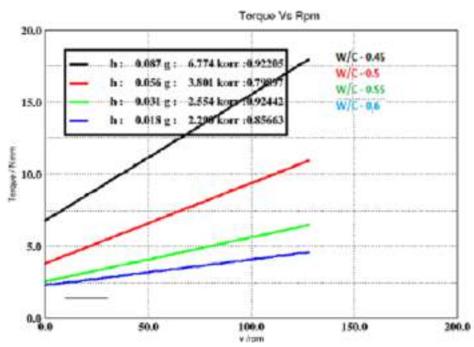

Figure 5.5: Bingham curve of cement paste with varying w/c ratio

Table 5.9: Rheological parameter of OPC-53

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	6.774	0.087	0.92205
0.5	3.801	0.056	0.79897
0.55	2.554	0.031	0.92442
0.6	2.290	0.018	0.85663

Table 5.10: Rheological parameter of Undensified Silica fume at 5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	20.197	0.172	0.62804
0.5	9.495	0.094	0.84873
0.55	4.813	0.064	0.89517
0.6	2.842	0.047	0.95879

Table 5.11: Rheological parameter of Undensified Silica fume at 7.5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	38.105	0.172	0.62804
0.5	17.023	0.136	0.82646
0.55	8.773	0.084	0.85779
0.6	4.588	0.062	0.81775

Table 5.12: Rheological parameter of Undensified Silica fume at 10% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	58.917	0.280	0.53925
0.5	28.911	0.197	0.54015
0.55	12.063	0.123	0.81303
0.6	6.773	0.074	0.92010

Table 5.13: Rheological parameter of Densified Silica fume at 5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	9.672	0.105	0.82209
0.5	5.189	0.057	0.96097
0.55	2.681	0.039	0.95890
0.6	1.932	0.024	0.91467

Table 5.14: Rheological parameter of Densified Silica fume at 7.5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	9.842	0.116	0.86807
0.5	4.854	0.063	0.92110
0.55	3.228	0.046	0.92874
0.6	2.091	0.025	0.90935

Table 5.15: Rheological parameter of Densified Silica fume at 10% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	10.072	0.127	0.86402
0.5	5.070	0.087	0.61119
0.55	2.903	0.049	0.94100
0.6	2.138	0.029	0.0.92970

Table 5.16: Rheological parameter of Metakaolin at 5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	21.007	0.130	0.78783
0.5	9.385	0.093	0.9024
0.55	5.52	0.052	0.93646
0.6	3.767	0.037	0.94303

Table 5.17: Rheological parameter of Metakaolin at 7.5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	31.288	0.120	0.94323
0.5	13.470	0.076	0.85875
0.55	8.095	0.051	0.91430
0.6	5.138	0.044	0.92470

Table 5.18: Rheological parameter of Metakaolin at 10% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	38.593	0.153	0.64743
0.5	21.597	0.101	0.72019
0.55	11.865	0.081	0.87234
0.6	7.193	0.052	0.88997

Table 5.19: Rheological parameter of Classified Fly Ash (P-100) at 5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	6.862	0.083	0.88397
0.5	3.813	0.058	0.92292
0.55	2.389	0.036	0.93259
0.6	2.214	0.019	0.861262

Table 5.20: Rheological parameter of Classified Fly Ash (P-100) at 7.5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	7.357	0.093	0.85340
0.5	3.952	0.057	0.94135
0.55	2.492	0.035	0.97022
0.6	1.893	0.020	0.89363

Table 5.21: Rheological parameter of Classified Fly Ash (P-100) at 10% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	7.234	0.091	0.81484
0.5	3.53	0.055	0.90419
0.55	2.224	0.035	0.91537
0.6	2.079	0.022	0.90808

Table 5.22: Rheological parameter of Ground Fly Ash at 5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	8.583	0.098	0.70768
0.5	4.662	0.071	0.68529
0.55	2.763	0.042	0.86056
0.6	2.283	0.024	0.88757

Table 5.23: Rheological parameter of Ground Fly Ash at 7.5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	9.9293	0.105	0.78741
0.5	5.434	0.075	0.53658
0.55	2.642	0.047	0.79574
0.6	1.952	0.032	0.86211

Table 5.24: Rheological parameter of Ground Fly Ash at 10% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	10.012	0.132	0.5006
0.5	5.112	0.062	0.97277
0.55	2.595	0.046	0.99200
0.6	2.124	0.035	0.85208

Table 5.25: Rheological parameter of Micro Talc at 5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	8.275	0.090	0.80777
0.5	4.427	0.053	0.98722
0.55	2.773	0.036	0.90927
0.6	2.315	0.02	0.97289

Table 5.26: Rheological parameter of Micro Talc at 7.5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	9.189	0.095	0.78944
0.5	5.099	0.049	0.92243
0.55	3.371	0.032	0.91532
0.6	2.276	0.026	0.97922

Table 5.27: Rheological parameter of Micro Talc at 10% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	10.564	0.082	0.81177
0.5	6.153	0.053	0.87367
0.55	3.862	0.035	0.91435
0.6	2.779	0.027	0.90814

Table 5.28: Rheological parameter of Alccofine at 5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	9.332	0.089	0.88382
0.5	4.658	0.051	0.95281
0.55	2.928	0.036	0.94048
0.6	2.187	0.026	0.91006

Table 5.29: Rheological parameter of Alcco fine at 7.5% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	10.045	0.104	0.84891
0.5	5.628	0.069	0.78898
0.55	3.056	0.042	0.92918
0.6	2.319	0.030	0.93456

Table 5.30: Rheological parameter of Alccofine at 10% replacement

w/c ratio	Yield stress (N.mm)	Viscosity (N.mm.min)	R^2
0.45	12.813	0.129	0.86939
0.5	6.329	0.065	0.92493
0.55	3.544	0.044	0.93312
0.6	2.191	0.034	0.94592

5.2.1 Effect of Microfine Additives on Rheological Parameter

In Fig5.6-5.11 the yield stress and viscosity are shown for mixtures composed of cement paste with the different w/c ratio of 0.45, 0.5, 0.55,and 0.6. The amounts of the various mineral admixtures by mass as replacement of cement are indicated on the figure.

It is clear that the replacement of cement with Classified Fly Ash (P-100) leads to a decrease in the yield stress while viscosity shows complex behavior.Micro Talc shows decreases in viscosity at w/c ratio 0.5 and 0.55 and Classified Fly Ash shows decreases in viscosity at w/c 0.45 and 0.6.In contrast, the replacement of cement by Undensified Silica fume and Metakaolin significantly increases a yield stress and viscosity.

Therefore it is also clear that the Undensified Silica fume and Metakaolin requires high dosages of HRWR while Classified Fly Ash requires lesser dosages of HRWR or no dosages of HRWR for given yield stress or viscosity compare to control.

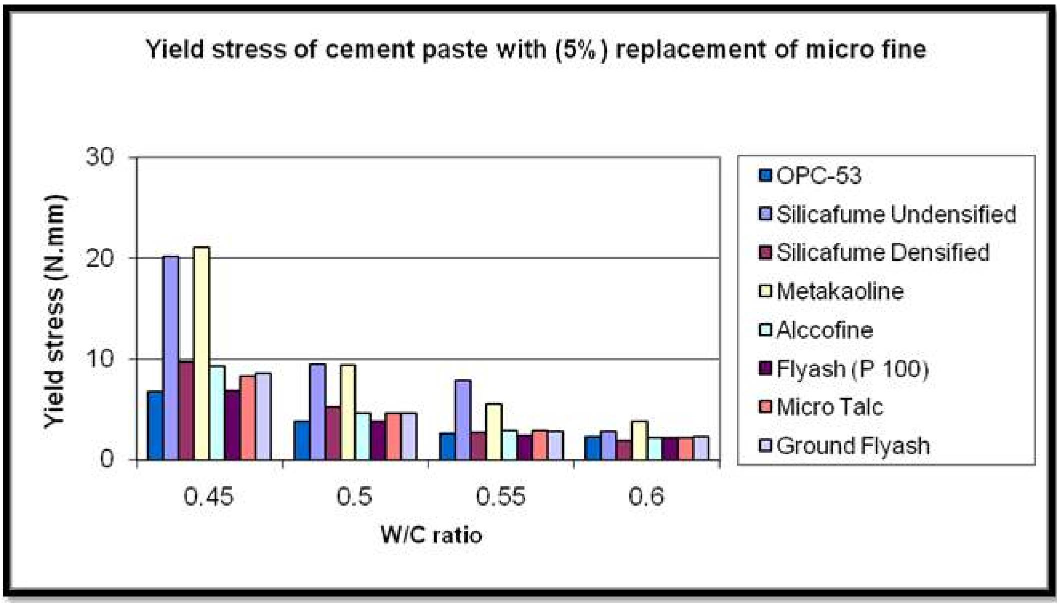

Figure 5.6: Effect of Micro-fines mineral admixture (5%) replacement on Yield Stress

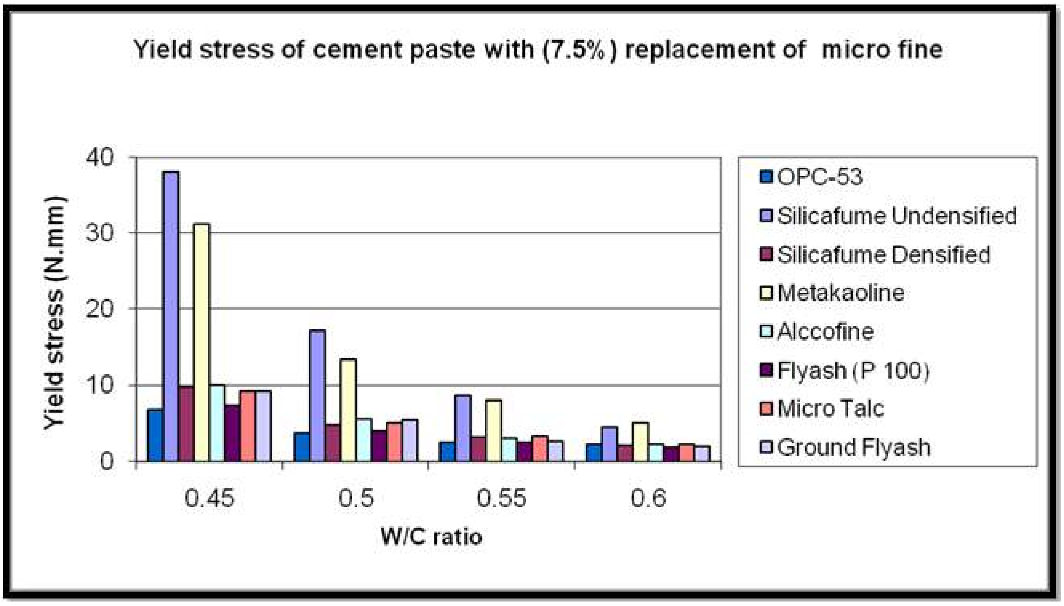

Figure 5.7: Effect of Micro-fines mineral admixture (7.5%) replacement on Yield stress

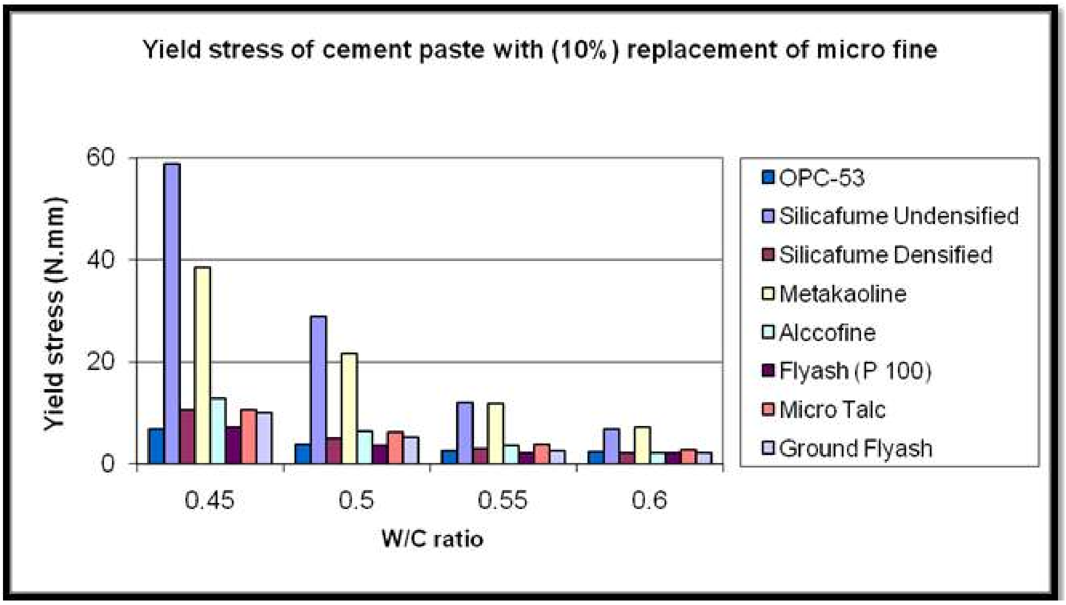

Figure 5.8: Effect of Micro-fines mineral admixture (10%) replacement on Yield stress

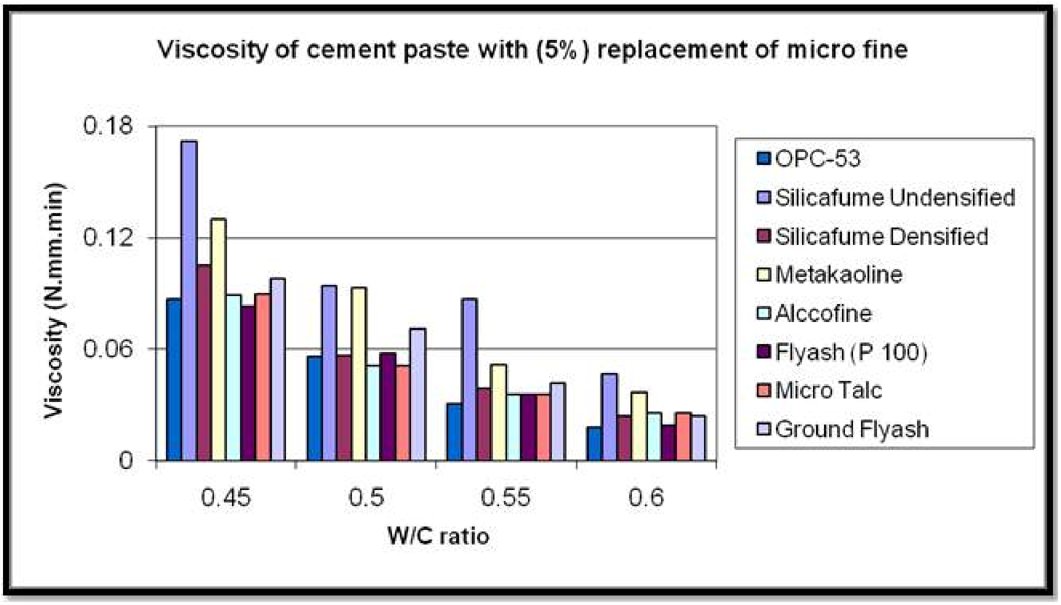

Figure 5.9: Effect of Micro-fines mineral admixture (5%) replacement on Viscosity

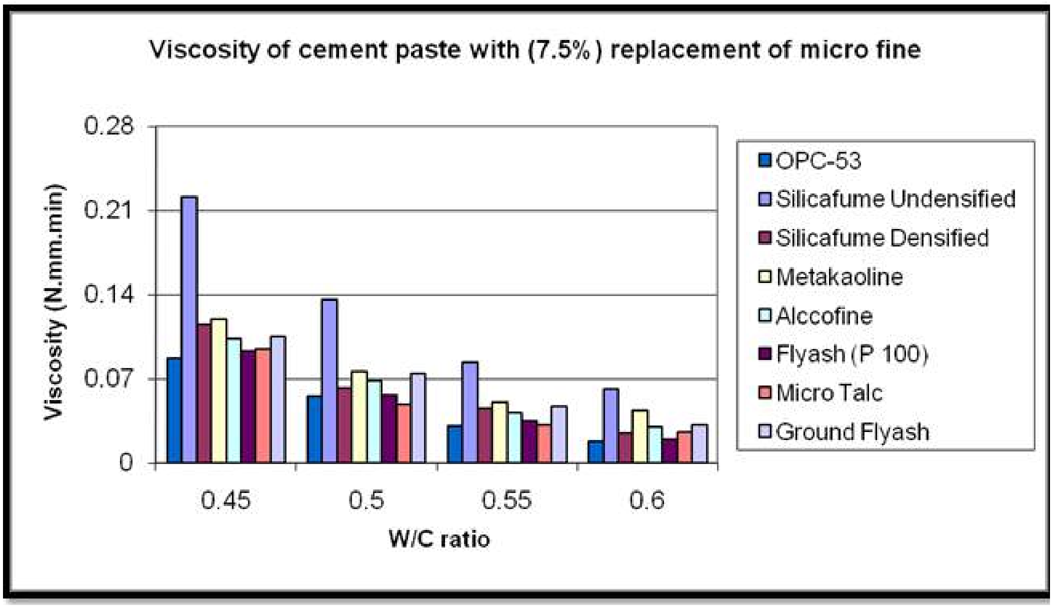

Figure 5.10: Effect of Micro-fines mineral admixture (7.5%) replacement on Viscosity

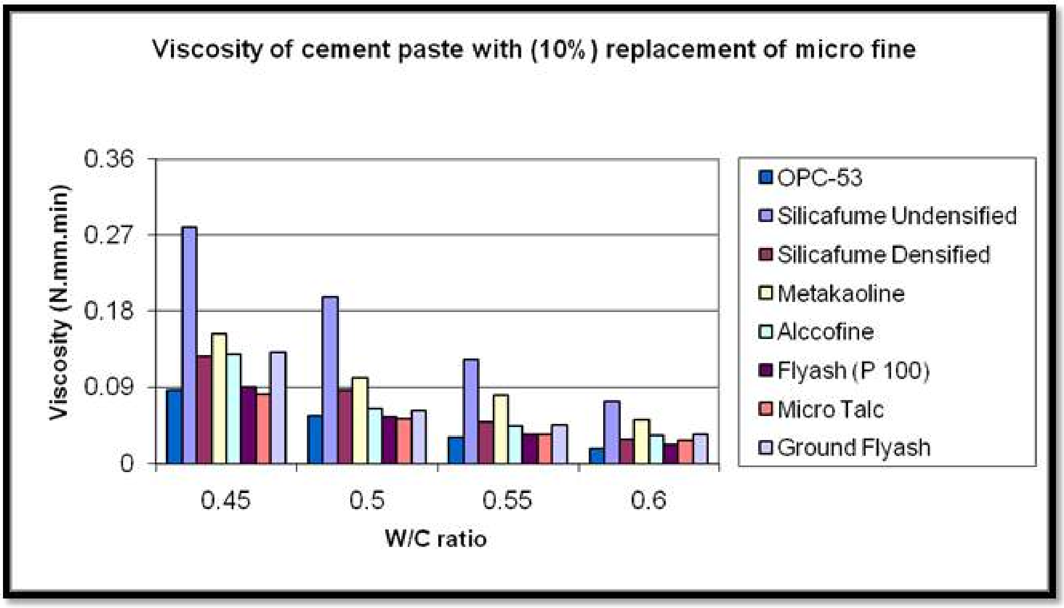

Figure 5.11: Effect of Micro-fines mineral admixture (10%) replacement on Viscosity

5.3 Evaluation of Co-relation between Yield stress and Minislump flow of Cement Paste

This section contains result of co-relation between yield stress and Minislump flow diameter of cement paste with different dosage of micro-fines mineral admixture are presented.This results are important because fluid rheometer for cement paste is not widely available in the construction industry.
The main reasons are: the instrument cost and the importance of using such a device for cement paste was not advocated.If relationship could be established, the empirical tests could be used to design materials for a given yield stress. Fig 5.12- 5.19 shows the co-relation factor between yield stress and minislump flow of different microfines.

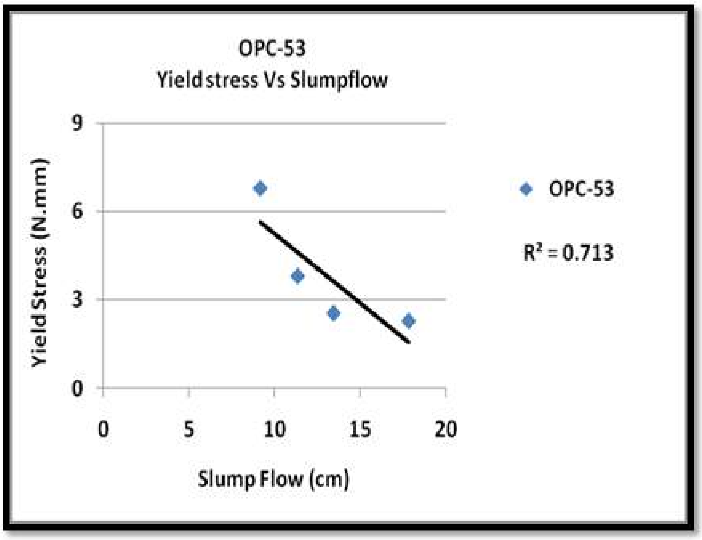

Figure 5.12: Co-relation between Yieldstress and Minislump flow of OPC-53

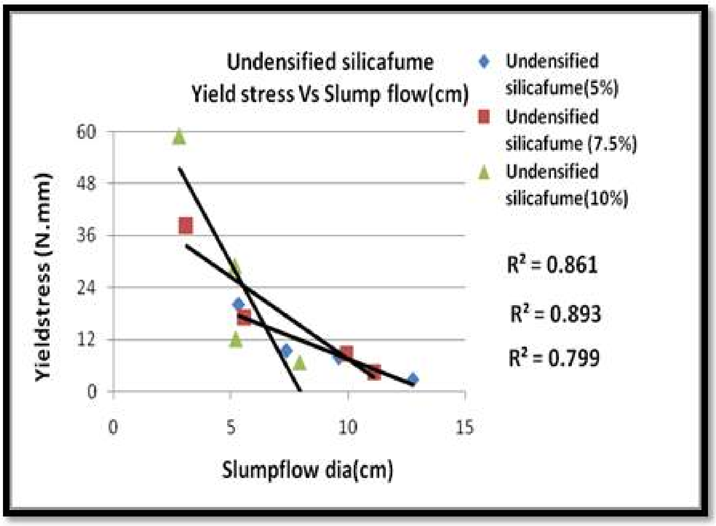

Figure 5.13: Co-relation between Yieldstress and Minislump flow of Undensified Silica fume

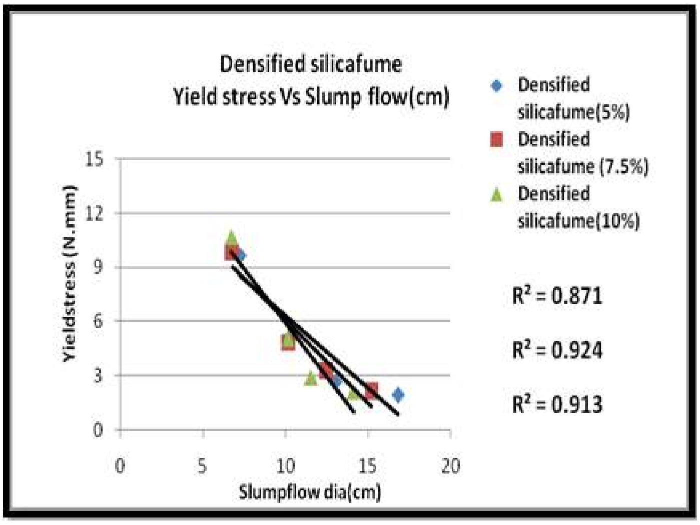

Figure 5.14: Co-relation between Yieldstress and Minislump flow of Densified Silica fume

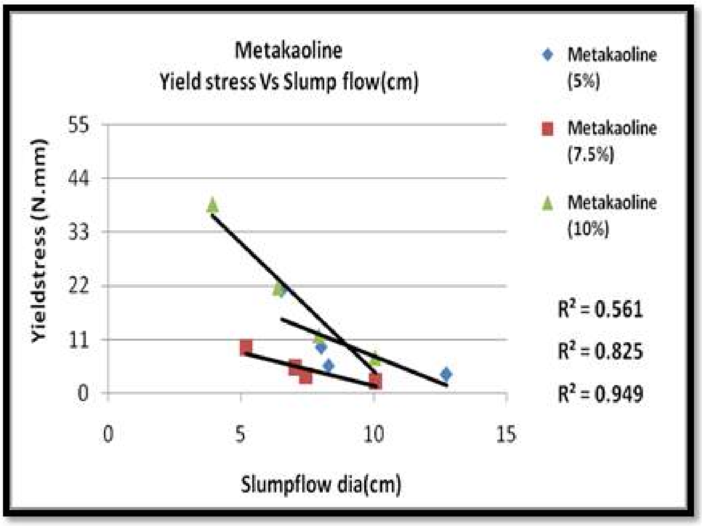

Figure 5.15: Co-relation between Yieldstress and Minislump flow of Metakaolin

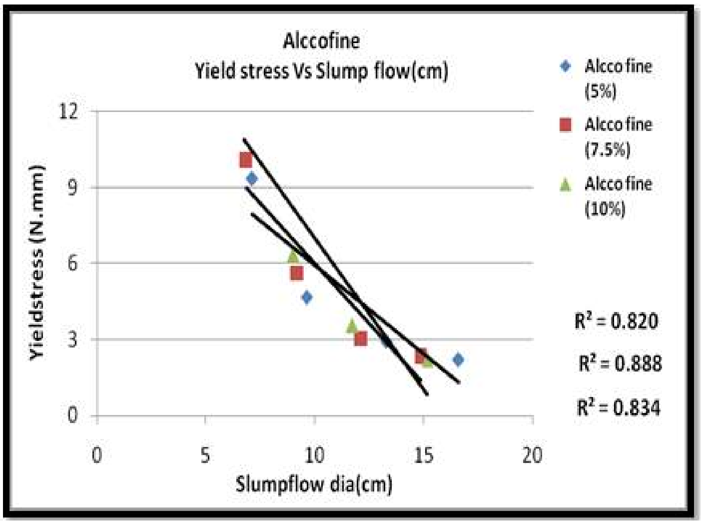

Figure 5.16: Co-relation between Yieldstress and Minislump flow of Alcco fine

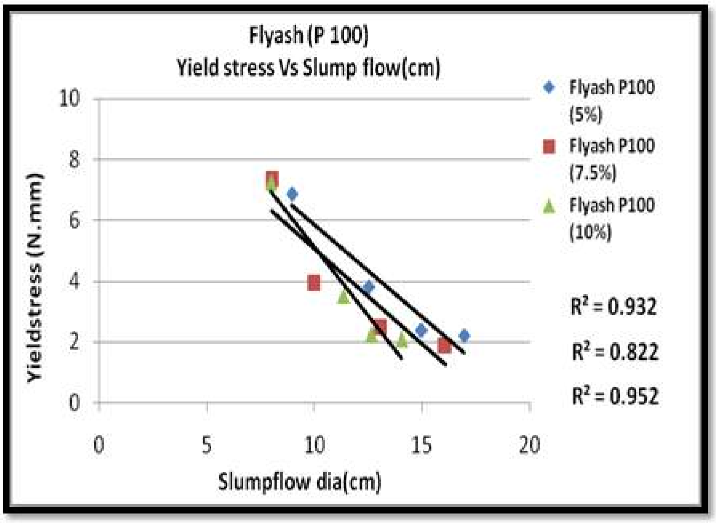

Figure 5.17: Co-relation between Yieldstress and Minislump flow of Classified Fly Ash(P-100)

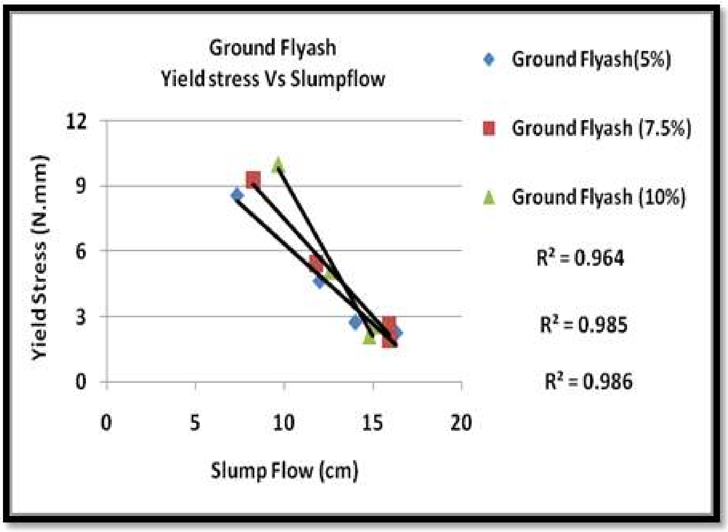

Figure 5.18: Co-relation between Yieldstress and Minislump flow of Ground Fly Ash

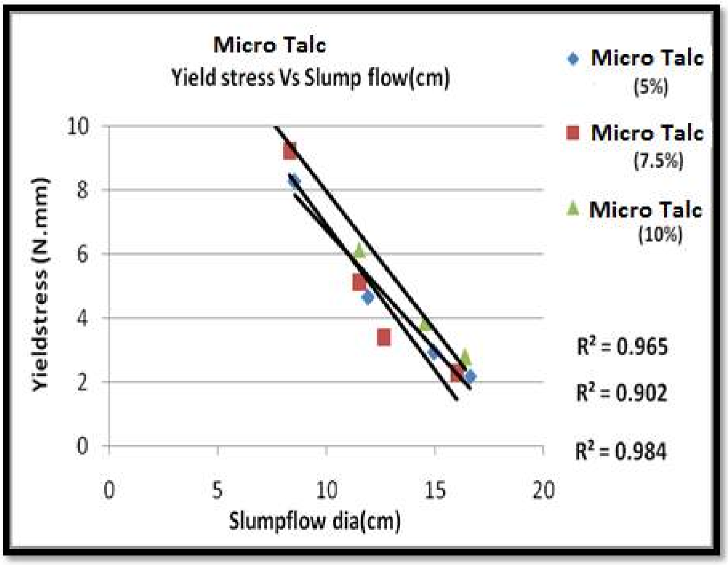

Figure 5.19: Co-relation between Yieldstress and Minislump flow of Micro Talc

From the Fig5.20 its shows that co-relation factor between yield stress and slump flow of different micro-fines are near about 0.9 but,Ground Fly Ash and Micro Talc is greater among the all other micro-fines at dosages of 5% , 7.5% and 10% replacement of cement by mass. In contrast Metakaolin shows poor co-relation factor at dosage of 5% replacement.

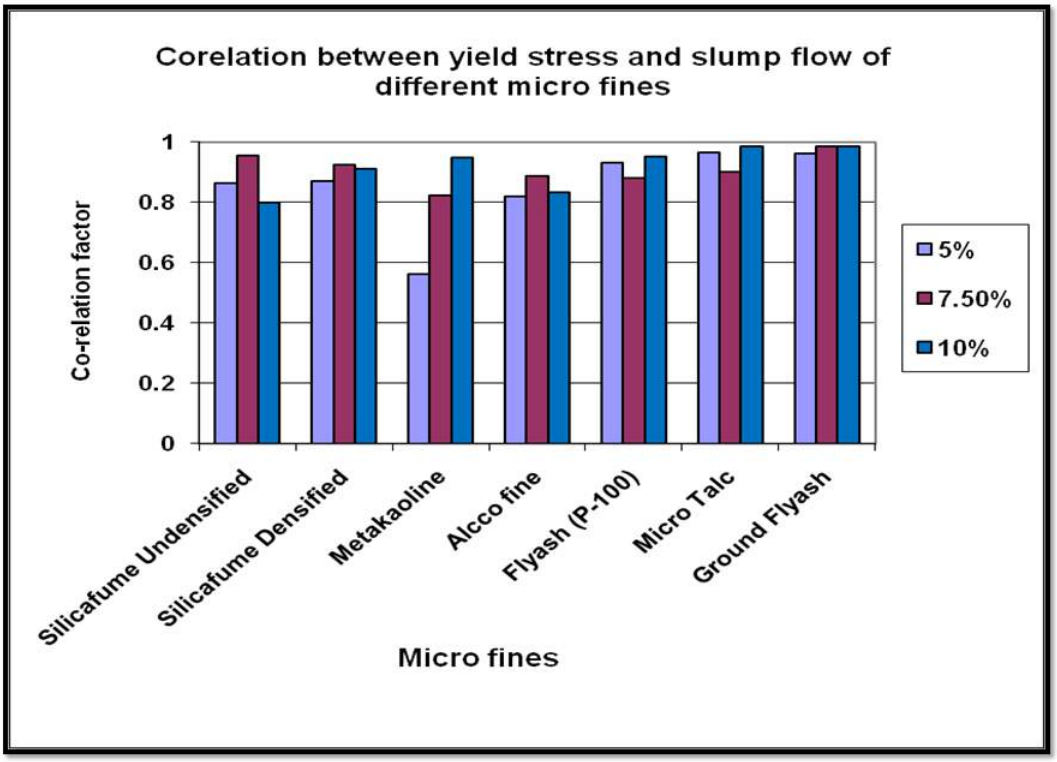

Figure 5.20: Co-relation factors of diffrent Microfines

5.4 Zeta Potential Test

This test is conducted to check the zeta potential of all microfine mineral admixtures. This test is performing on zeta potential analyzer for 30 mins. Results of zeta potential of microfine mineral admixtures are shown in Table5.4. All the mix are prepared in double distilled water. Rheobuild 1100 Type-F super plasticizer is also used to compare with microfines plasticizing effect.

There are three methods are available for measurement of Zeta potential.

- Optical Methods
- Acoustic Methods
- Streaming Potential Methods.

Streaming Potential Methods.
Zeta Potential Analyzer is working by this method and calculate the value of zeta potential.

- Measurement of potential (U_{st}) generated from liquid flow through surfaces of charged particles.
- More suitable for fiber, porous materials, and solid surfaces.
- Produce an average zeta potential.

$$\frac{U^{st}}{\Delta P} = \frac{\varepsilon\zeta}{\kappa\eta} \tag{5.1}$$

ΔP= flow pressure difference

η =medium viscosity;

ε = medium permittivity

κ_m =conductivity for medium

ζ = Zeta Potential (mV).

Table 5.31: Zeta Potential Value of Different Microfines

Particulars	Zeta Potential (mV)
1% Super Plasticizer	-39.7
Undensified Silica fume	-14.1
Densified Silica fume	-14
Metakaoline	-17.4
Alccofine	-16.4
Classified Fly Ash(P-100)	-21.2
Ground Fly Ash	-9.6
Micro Talc	11.3

From the Fig5.21 shows that Classified Fly Ash shows higher value of zeta potential (-21.2 mV) compared to other microfines while 1% SP shows value of zeta potential is (-39.7 mV). Silica fume is having a lower value of zeta potential (-14 mV). Micro Talc is having a zeta potential value 11.3 mV;positive value of zeta potential represents the electro-static attractive force.

The negative value of zeta potential represents that electro-static repulsive force. Classified Fly Ash (P-100) shows closer value of zeta potential with respect to super plasticizer value of zeta potential. It shows some plasticizing effect is present in Classified Fly Ash (P-100).

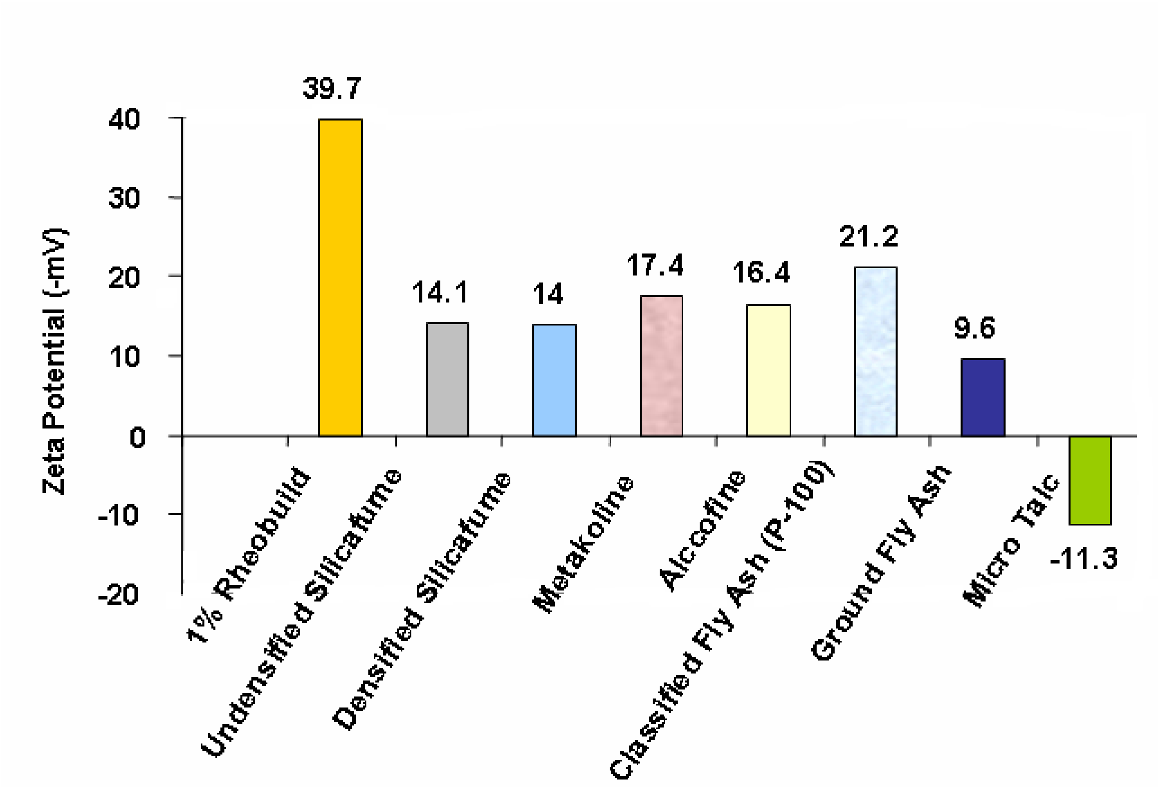

Figure 5.21: Zeta Potential Value of Microfine Additives

5.5 Possible Reasons for Impact on Rheological Properties of Cement Paste due to Micro fines Additives.

The possible reason of Undensified Silica fume for increasing in rheological parameter is its extreme fineness and very high amorphous silicon dioxide content, makes silica fume highly reactive pozzolanic material while Fly Ash having lower silicon dioxide content makes Fly Ash lower reactive.

To enhance the performance of Fly Ash with increasing fine particles, so that it too function as a highly reactive pozzolana. Increasing the fineness of Fly Ash particles by grinding improves reactivity but eventually increased in water demand by irregularly shaped Ground Fly Ash particles while increasing the fineness of Fly Ash by air classification techniques improved reactivity of Fly Ash without impact on spherical shape of particles.

Secondly, a popular hypothesis for the rheological properties offered by Fly Ash states that Fly Ash spherical particles can easily roll over one another, reducing interparticle friction. It is also observed that Fly Ash(P-100) has a higher proportion of spherical particles than its parent Fly Ash. The use of microfines Classified Fly Ash also broadens the particle size distribution of over all cementitious system, thus potentially improving packing features. Higher packing densities and increased sphericity in theory,should result in an increased availability of free water, leading to improved workability or rheology.

From the zeta potential test; Classified Fly Ash shows higher value of zeta potential (-21.2 mV) compared to other microfines while 1% SP shows value of zeta potential is (-39.7 mV). It represents that Classified Fly Ash (P-100) particles adsorbs on the cement grains particle and creates electro-static repulsive force which overcomes the attractive force and having some plasticizing effect which is the reason for improvement in rheological behavior of cement paste.

Silica fume is having a lower value of zeta potential (-14 mV) that represents poor performance in rheological behavior. Micro Talc is having a zeta potential value 11.3 mV; positive value of zeta potential represents the electro-static attractive force but steel Micro Talc showing good rheological behavior. The reason for that is Micro Talc having lower silica content and only used for filling material there is no role plays in hydration process.

Chapter 6

Evaluation of Durability Properties of Cement Mortar

This chapter contains test results and discussion of durability properties like rapid chloride permeability test and chloride migration test for different types of micro-fines mix mortar.

6.1 Compressive Strength

For compressive strength of cement mortar; same mix proportion is used which is used in RCPT test and chloride migration test. Results of compressive strength of cement mortar are presented in Table6.1

Table 6.1: Compressive Strength of Microfines

Particulars	**Compressive Strength (MPa)**
OPC-53	59.031
Undensified Siicafume	80.83
Densified Silicafume	71.02
Metakaolin	65.52
Alccofine	74.31
Classified Fly Ash (P-100)	66.29
Ground Fly Ash	64.72
Micro Talc	59.52

6.2 Rapid Chloride Permeability Test (RCPT)

Tests has been performed to study the chloride ion permeability property of different types of micro-fines mortar mixes. The details of the tests are described in chapter 3.

The chloride ion permeability has been evaluated based charged passed,quality of concrete after the exposure of alkaline solution up to 6-hours time period at 60 V of all the micro-fines mixes.Specimen of all the mortar mixes have been cured at at 25'C for 28 days. If the current is recorded at 30 min intervals, the following formula, based on the trapezoidal rule, can be used to perform the integration:

$$Q = 900(I_0 + 2I_{30} + 2I_{60} + ... + 2I_{300} + 2I_{330} + I_{360}) \tag{6.1}$$

Where: Q = charge passed (coulombs), I_o = current (amperes) immediately after voltage is applied, and I_t = current (amperes) at t min after voltage is applied.

Result of charged passed in all microfines and penetrability class are shown in Table 6.2

Table 6.2: RCPT Test Results of Micro-fines mix

Micro-fines Mortar Mixes	**Specimen No.**	**Charged passed (Columbus)**	**Average**	**Chloride Penetrability Class**
OPC-53	1	2898.5	2905	Moderate
	2	2905.3		
	3	2911.2		
Undensified Silicafume	1	544	516	Very low
	2	506.6		
	3	497.4		
Densified Silicafume	1	842.03	865.33	Very low
	2	888.63		
	3	865.33		
Metakaolin	1	1404.79	1224.29	Low
	2	1331.03		
	3	937.07		
Alccofine	1	5604.34	4833.5	High
	2	4301		
	3	4595.27		
Classified Fly Ash (P-100)	1	3507.8	3619.2	Moderate
	2	3734.6		
	3	3615.32		
Ground Fly Ash	1	4120	3722.09	Moderate
	2	3456.12		
	3	3581.17		
Micro Talc	1	3403.31	3594.82	Moderate
	2	3684.06		
	3	3697.13		

From the Fig. 6.1 It can be observed that mix with Silicafume gives the lower value of charge passed and very low penetrability class while mix with Alccofine gives the higher value of charge passed and high penetrability class. Metakaolin mix specimen gives low class of penetrability while Ground Fly Ash, Classified Fly Ash and Micro Talc gives moderate type of penetrability class. In contrast the magnitude of charge passed is vary for all the micro fines though its penetrability class is same.

Charge passed value of mixture with Undensified Silicafume is 516 Coulombs compared with 2905 Coulombs of control sample at 28 days. This represents an decrease to almost 82% in the chloride permeability. In contrast Alccofine mix shows 4833.5 Coulombs compared with 2905 Coulombs of control sample at 28 days. This represents an increase to almost 66 % in the chloride permeability. This may result, however, from a change in the ionic concentration of pore solution rather then a change in pore structures.

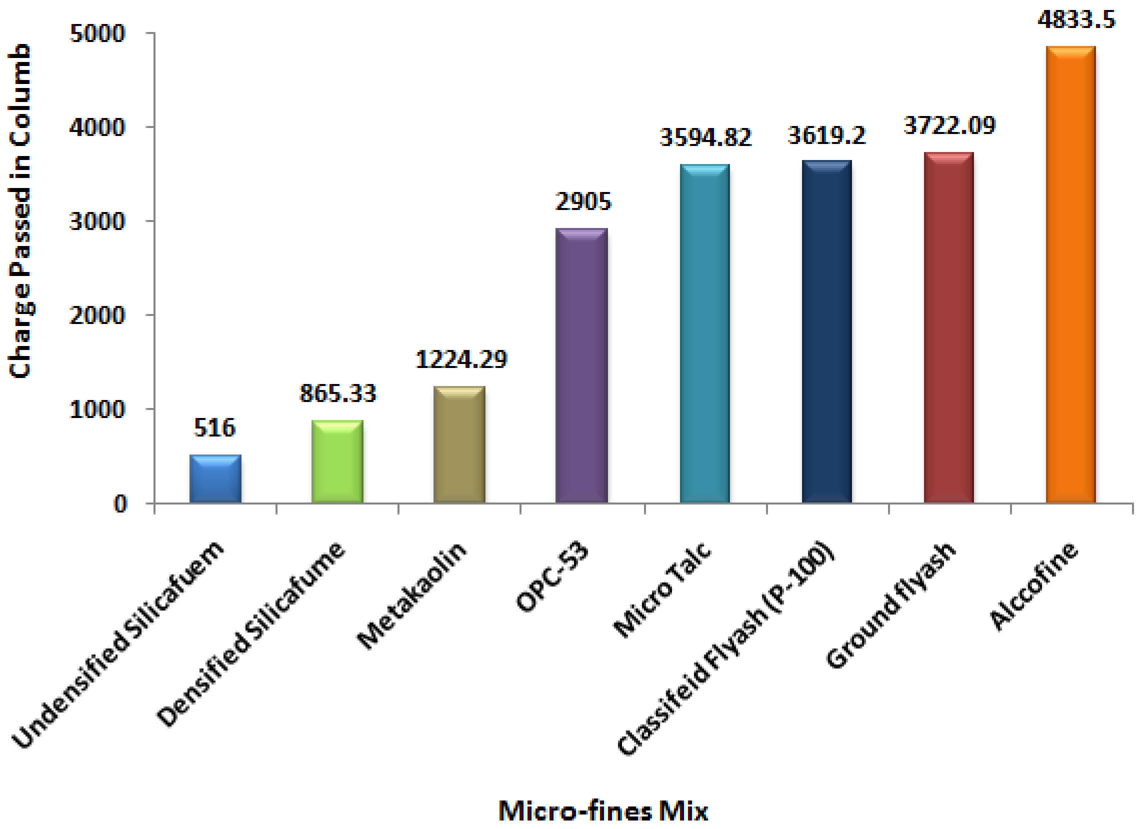

Figure 6.1: RCPT value of different micro-fine mix mortar

6.2.1 Limitation of RCPT:

The test principles are quit different to the mechanisms that govern the penetration of chlorides in concrete in real life, which are:

- Diffusion
- Capillary suction
- Permeability

All of them are very closely dependant on the pore structure of the concrete and only to a minor extent to the chemistry of the pore solution.

The RCPT measures the electrical conductivity of specimen i.e current passing under given voltage. Now, very important to stress the current passing is just not contributed by Cl^- ions migrating from the cathode to the anode, but also by the movement of all the ions that are in the pore solution of concrete (OH^-, Na^+, K^+, ${SO_4}^{-2}$). Not all the ions carry the same amount of current, as this dependant of the individual ionic mobility. For instance, the ion equivalent conductivity of OH^- is 0.0198 m^2/equiv.ohm, whilst that of Cl^- is just 0.00763, see the Table6.2.1. Hence, in the case of concrete, usually the main proportion of the current is attributable to the OH- ions rather than to Cl^-.

Table 6.3: Conductivity of Different ions

Particulars	**Conductivity (m^2/equiv.ohm)**
Na^+	0.00501
K^+	0.00735
Ca^{+2}	0.00595
${SO_4}^{-2}$	0.00798
OH^-	0.0198
Cl^-	0.00763

As a result the outcome of the RCPT is strongly affected by the chemistry of the pore solution that in turns, depends on the cement chemistry and very much on the content and characteristics of mineral components in the cement or added additives.

6.3 Chloride Migration Test

This tests has been performed to study the chloride ion migration property of different types of micro-fines mix mortar. For depth measurement silver nitrate solution is sprayed on the one of the splited sample and measured the depth of white precipitates with calipers Fig.6.2 shows the silver nitrate sprayed specimen. Specimen of all the mortar mixes have been cured at at 25'C for 28 days. Calculate the chloride migration co-efficient as given in Appendix A. Result of chloride penetration depth and co-efficient of chloride migration is presented in Table6.3.

Figure 6.2: Test Specimen After Silver Nitrate Spray

Table 6.4: Chloride Migration Test Results of Micro-fines mix

Mortar Mixes	**No.**	**Penetration Depth (mm)**	**Chloride Migration Co-efficient in 10^{-12}**	**Average in 10^{-12}**
OPC-53	1	18.18	8.65	8.71
	2	20.13	8.56	
	3	19.23	8.91	
Undensified Silicafume	1	5.68	2.36	2.45
	2	6.27	2.73	
	3	5.43	2.25	
Densified Silicafume	1	7.68	3.55	3.95
	2	7.52	3.54	
	3	10.023	4.77	
Metakaolin	1	13.51	6.49	5.54
	2	11.59	5.29	
	3	10.82	4.86	
Alccofine	1	27.57	14.6	12.83
	2	24.51	12.7	
	3	22.34	11.2	
Classified Fly Ash (P-100)	1	24.02	11.8	14.53
	2	38.39	19.4	
	3	24.14	12.4	
Ground Fly Ash	1	22.08	10.7	14.27
	2	28.31	14.4	
	3	35.83	17.7	
Micro Talc	1	21.19	11.3	11.3
	2	24.12	11.8	
	3	22.88	10.8	

From the Fig. 6.3 shows that Undensified Silicafume gives lower value of chloride migration co-efficient while Classified Fly Ash and Ground Fly Ash shows the higher value of chloride migration co-efficient compared to control. The value of OPC-53 (control) sample is 8.71×10^{-12} while Undensified Silicafume gives value of chloride co-efficient is 2.45×10^{-12}. It represents that value decrease to 72 %. For Classified Fly Ash (P-100) and Ground Fly Ash shows value accordingly 14.53, 14.27×10^{-12}. It represents that value increases to 67 %.

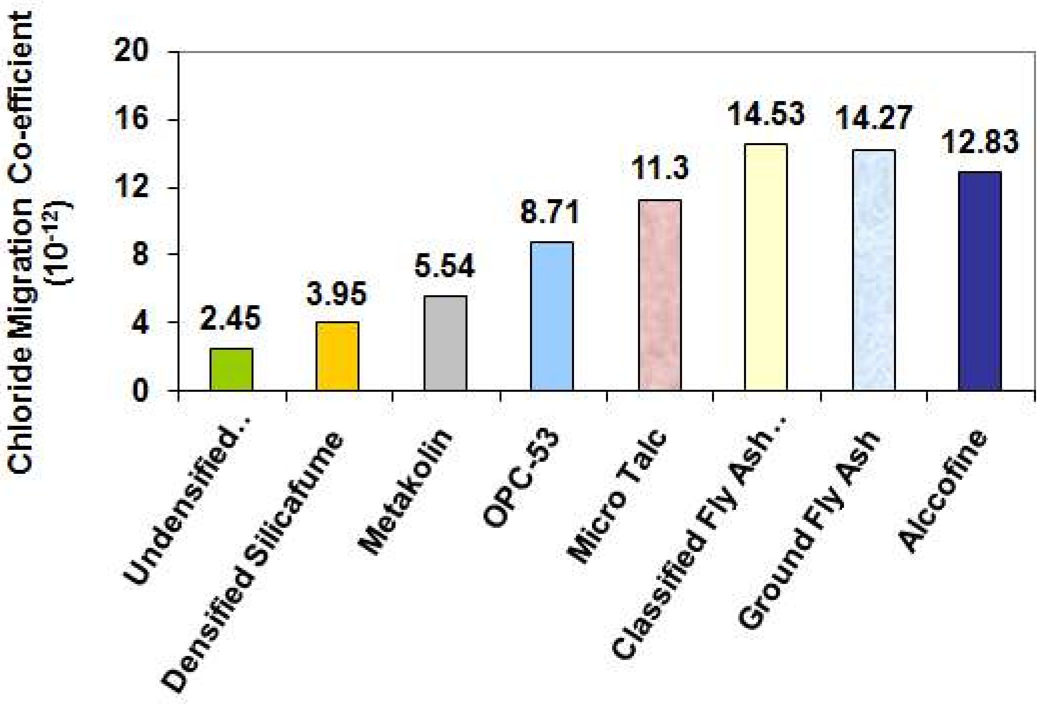

Figure 6.3: Chloride Migration Co-efficient Value of Micro-fine Mix Mortar

6.4 Comparison Between RCPT and Chloride Migration Test

RCPT test determine the electrical conductance of concrete to provide a rapid indication of its resistance to the penetration of Chloride ions. But ASTM C-1202 is stated that method is applicable to types of concrete where correlation have been established between this test procedure and long term chloride ponding procedures such as those describe in ASTM C- 1556 and AASHTO -T-259. To overcome the limitation of ponding test long time duration; chloride migration test is developed and co-relate with RCPT.

From the comparison between RCPT charged passed value and chloride migration co-efficient value shows good co-relation between them. The value of co-relation factor is around (R^2 = 0.88). This shows that both tests are confirmative test. Same behaviors of the micro fines are seen for the resistance of chloride ion permeability and the rate of chloride ion travel. There is no contradictory behavior is noted for any micro-fine additives.

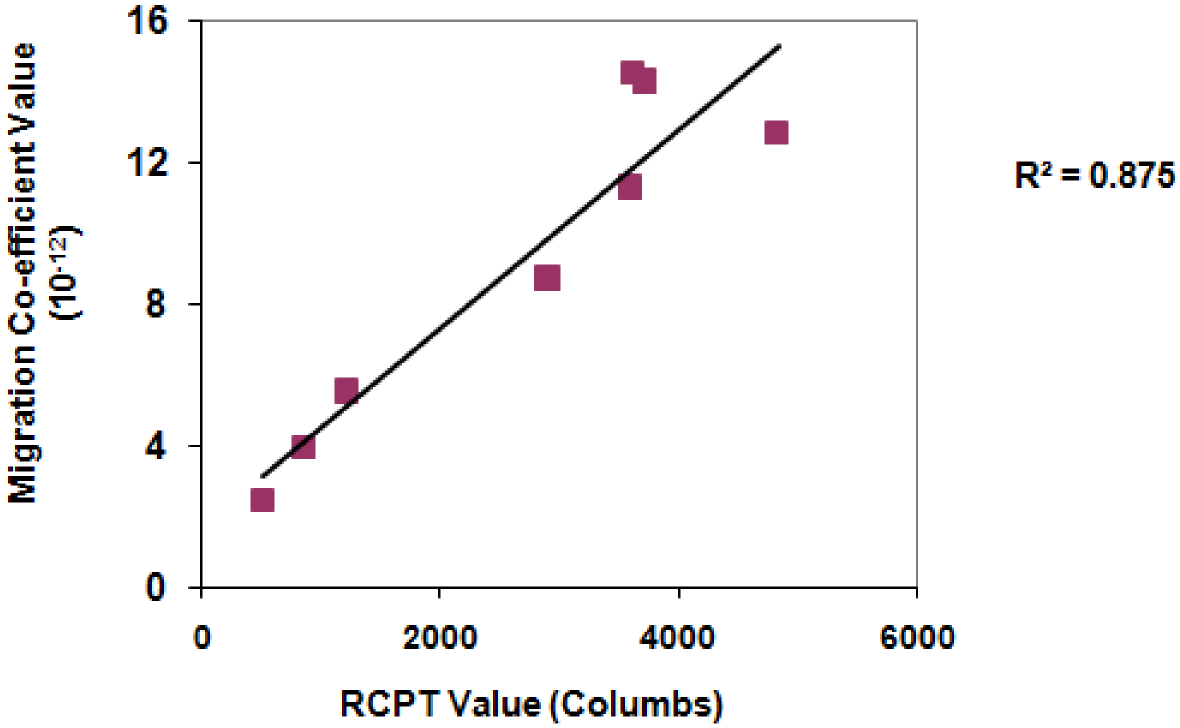

Figure 6.4: Co-relation Between RCPT Value and Chloride Migration Co-efficient Value

6.5 Possible Reasons for Impact on Durability Properties of Cement Mortar due to Micro fines Additives.

It is known that permeability of concrete or mortar is decreases by some extent by incorporating mineral admixture into the cement.

For every mineral admixture there is some threshold value are decided to improve the properties of incorporated material. The threshold value of Silicafume and Metakaolin are 5-10 % replacement or addition by mass of cement while for Fly Ash has threshold limit up to 20%and for the Slag the limit is up to 50%.

So, that is one of the reasons for showing the poor durability properties in terms of chloride ion resistance. Indeed Second reason for Fly Ash showing poor performance against chloride ion resistance is Fly Ash takes longer time for complete hydration process.

Chapter 7

Concluding Remarks and Future Scope of Work

7.1 Summary

The rheological and durability properties of seven types of micro-fine additives have been studied in the present investigation. The rheological properties included in this study are mini-slump flow, rheological parameters like yield stress and viscosity. The durability properties included are rapid chloride permeability and chloride migration.

For understanding about terminology, rheological testing process of cement paste, effect of various parameters on rheological properties of cement paste, and durability properties of micro-fine mineral admixtures etc. information available in literature has been studied.

For investigation of rheological properties of micro-fine additives namely, Silicafume, Metakaolin, Alccofine, Fly Ash, and Micro-Talc has been selected. First chemical properties and physical properties like specific surface, particle size distribution and compressive strength of all the micro-fines are evaluated.

Preliminary investigation is conducted to evaluate the effect of mineral admixture on rheology of cement paste and also to check the reliability of empirical rheological test to fundamental rheological test.

Based on preliminary investigation, seven types of micro-fine materials are selected for further investigation of rheological property with four different dosages of w/c ratio and three different dosages of micro-fine mineral admixtures. For mixing of cement paste digital mortar mixture is used.

For rheometer test step profile in decreasing order is selected i.e (120,100,80,60,40 RPM) with each step lasting for 5 min. Total duration of test is 25 min. After completing the experiment, the curve between torque vs rpm is plotted and fitted the straight line as per the bingham model. Yield stress from the intercept of the straight line and viscosity from the slope of the straight line is measured.
For mini-slump test; cement paste with different w/c ratio and different dosage of microfines is prepared. After mixing the cement slurry in the Mini Slump cone is poured. The cone is lifted and the flow diameter of the slurry in all four direction is measured. Average of all four diameter of cement slurry.

For durability test of micro-fine mineral admixtures two types of durability test is selected based on their importance. First is rapid chloride permeability test and the second is chloride migration test.

Mix proportion of cement mortar has been prepared for investigation of durability properties. Mix proportion of cement mortar is kept as (1:3) mix, where replacement of micro-fines are 7.5 % to the mass of cement and w/c ratio is kept as 0.4. Digital mortar mixture is used for mixing of mortar. After casting the cylindrical specimen of 100 mm diameter and 200 mm height, the specimens are cured for 28-days.

For rapid chloride permeability test two types of alkaline solution is used for cathode and anode. In cathode 3% NaCl solution by weight is used and in anode 0.3 N NaOH solution is used. This test is running for 6-hr and charge passed from the 100mm diameter and 50 mm thick specimen is calculated as per the ASTM- C-1202 [24]. Voltage supply is kept 60V.

For chloride migration test alkaline solution used for the cathode is 10% Nacl solution by weight, anode solution is same as used in RCPT test. This test is running for 24-hr and voltage supply is kept 30V. After completing the test for 24-hr split the sample axially and the silver nitrate solution is sprayed on the surface of the one splited sample after 15 min. White precipitation is formed. The depth is measured and the chloride migration co-efficient is calculated as per the NT Build-492.

7.2 Concluding Remarks

Following concluding remarks have been made on basis of the work conducted in the major project:

Preliminary Investigation of Rheology of Cement Paste

- It was determined that mix with Fly Ash (30% repalcement) shows higher minislump flow diameter compared with other cement paste. On the other hand OPC + Fly Ash shows lower value of minislump flow diameter compare to OPC-53 minislump flow diameter.

- In contrast marsh cone test shows no clear effect of mineral admixture on flow time Fly Ash mix shows longer time for w/c ratio 0.55 and 0.6 while slag mix shows longer time at w/c ratio 0.5.

- From the rheometer test it was determined that portland pozzolana cement shows higher yield stress value while OPC + Fly Ash mix shows lower value of yield stress compared with other cement paste. On the other hand yield stress value of OPC + Fly Ash mix shows higher value compared to OPC-53.

- In contrast viscosity shows complex behavior OPC + Fly Ash mix shows higher value of viscosity at w/c ratio 0.5 and 0.55 compared with other cement paste.
- Co-relation between empirical test and fundamental rheological test shows that co-relation between marsh cone flow time and viscosity shows no linear co-relation while minislump flow diameter and yield stress shows good linear co-relation factor.
- It is observed that mix with 30% Fly Ash shows lower value of yield stress compared to other mineral admixtures.

Rheological Properties of Cement Paste

- In cement paste,several microfine additives were examined. It was determined that mixtures with Classified Fly Ash (P-100) represented the best rheological improvement in terms of decreasing yield stress and viscosity. On the other hand Undensified Silica fume represented the worst. Undensified Silica fume shows significant increase in yield stress and viscosity. It can be conclude that the replacement of cement by Undensified Silica fume results in an increase in the water demand to maintain the rheological properties of the control.
- Less sophisticated test,such as the minislump test results of microfines shows good correlation with the yield stress measured by viscometer. Therefore, relationship between yield stress and minislump flow is advantageous to design material at a given yield stress.
- Classified Fly Ash shows the improved rheological performance compared to other microfine materials. So, Classified Fly Ash is the most preferred material for improving rheological performance of concrete during pumping.

Durability Properties of Cement Mortar

- At the age of 28 days mortar with silica fume shows very low penetrability class on the other hand mortar mix with Alccofine mix shows high penetrability class. Charge passed value of mixture with Undensified Silica fume is very lower while mix with Alccofine shows higher value. Other micro fines shows value of charged passed is in between Alccofine and Undensified Silica fume.

- At the age of 28 days same trend is observed in chloride migration co-efficient as observed in rapid chloride permeability test. The value of Undensified Silica fume shows lower value of migration co-efficient compared to control. On the other hand Classified Fly Ash and Ground Fly Ash shows higher value of co-efficient of migration. Other microfines shows value of chloride migration co-efficient in between Undensified Silica fume and Fly Ash.

- It is concluded from both the tests that almost similar kind of trend observed for chloride permeability and chloride migration test.

- For durability against chloride ion Silica fume is the most suitable material for use in construction application.

7.3 Future Scope of Work

The present study can be extended to include following aspects in the work.

- Investigation can be carried out on replacement of micro fine materials in to concrete to see the rheological behavior.

- Investigation can be carried out on effect of different types of chemical admixture with different dosages on rheology of cement paste and concrete.

- Study can be conducted by employing different types of rheometer on rheology of cement paste as well as concrete.

- Study can be carried out on developing co-relation between empirical test like slump flow test , v-funnel test etc. to rheometer test for self compacted concrete.
- Investigation can be carried out on evaluation of durability properties of concrete with replacement of all micro fine additives.
- Study can be conducted to check the other durability properties like water permeability; Acid resistance, Sulphate resistance etc. can also be studied for all micro fine additives.

Appendix A

Calculation of Chloride Migration Co-efficient

Calculation of co-efficient of chloride migration for OPC-53 cement mortar as per NT Build-492 are shown below:

z: absolute value of ion valence, for chloride, z = 1;

F: Faraday constant, F = 9.648 X 10^4 J/(VEmol);

U: absolute value of the applied voltage, V = 30 V;

R: gas constant, R = 8.314 J/(K.mol);

T: average value of the initial and final temperatures in the anolyte solution, K;

T = 298 K (25 'c)

L: thickness of the specimen in m; L = 0.051 m (51 mm)

$\mathbf{X}_d$: average value of the penetration depths in m; X_d = 0.01818 m (18.18 mm)

t: test duration, seconds; t = 86400 sec (24 hr)

$\mathbf{erf}^{-1}$: inverse of error function;

$\mathbf{c}_d$: chloride concentration at which the colour changes; 0.096 N for OPC concrete;

$\mathbf{c}_0$: chloride concentration in the catholyte solution; 2N for this test

Since $\mathbf{erf}^{-1}$ (1-$\frac{2X0.096}{2}$) = 1.25.

$$E_f = \frac{U-2}{L} \tag{A.1}$$

$E_f = \frac{30-2}{0.051} = 549.019$

$$\alpha = 2\sqrt{\frac{RT}{zFE}} erf^{-1}(1 - \frac{2C_d}{C_0}) \tag{A.2}$$

$\alpha = 2\sqrt{\frac{8.314X298}{1X9.648X10000X549.019}}$ X 1.25 = 2.405 X 10^{-6}

$$D_{nssm} = \frac{RT}{zFE}\frac{X_d - \alpha X_d}{t} \tag{A.3}$$

D_{nssm} = 8.65 X 10 $^{-12}$ m^2 $_/$ sec.

Appendix B

Analysis of Surface chloride content

The selected test specimens should be crushed with a hammer or similar tool to a size that no material is lost. The crushed material is then ground in the mill or grinder until a particle size less than 0.1 mm is obtained. Weigh the glass bottle. Insert about 5 g of sample into the glass bottle. Dry the sample at 105 ± 5 C until no reduction in weight can be seen (minimum 2 hours).

Before determining the weight of the dried sample, cool the glass bottle in a desiccator for not more than half an hour. Add about 20 ml of distilled water and shake the bottle to achieve separation of the particles. Add about 10 ml concentrated nitric acid, shake the bottle, add about 50 ml hot distilled water and shake again. Let the mixture cool for about one hour until it reaches ambient temperature.

Filter the solution and rinse the filter with 1 % nitric acid at least two times. All transitions of liquid should be followed by rinsing, at least twice, with 1 % nitric acid. This is very important to prevent loss of chlorides when you are working with low concentrations. Add distilled water until all the samples have the same volume.

Add silver nitrate solution in excess from the burette, about 10 ml is sufficient at low concentrations of chlorides. Add 23 ml benzyl alcohol or nonanol and 1 ml saturated ammonium ferri-sulphate solution. Insert the stopper into the bottle and shake so vigorously that the silver nitrate separates. Titrate the remaining amount of silver nitrate with the ammonium thiocyanate solution. Shake the bottle vigorously when the end point is near. Continue the titration at a slower rate during a continuously intensive mixing until the solution attains a permanent, weakly red colour.

The content of chlorides (Cl) is then calculated according to the formula:

$$Weightpercent Cl^{-} = 3.545 \times \frac{V_1 N_1 - V_2 N_2}{m} \tag{B.1}$$

V_1 = the added amount of silver nitrate solution (ml).
N_1 = the normality of the silver nitrate solution.
V_2= the added amount of ammonium thiocyanate solution during the titration (ml).
N_2 = the normality of the ammonium thiocyanate solution.
m = the weight of the sample (g).

Appendix C

List of Papers Published/Communicated

- Maulik M. Panseriya, Dr. Urmil V. Dave and Prof. Ashok K. Tiwari, ”Effect of Micro-fine Mineral Admixture on Rheology of Blended Cement Paste”, International Conference on Constructions Materials and Structures - 2014, Department of Civil Engineering Science, University of Johannesburg, Aukland Park, 24 - 26 November. (Paper Communicated)

- Maulik M. Panseriya, Dr. Urmil V. Dave and Prof. Ashok K. Tiwari, ”Effect of Fly Ash Fineness on Rheology of Cement Paste” , The 6th International Conference of Asian Concrete Federation - 2014, Asian Concrete Federation, Ganganam-gu, Seoul, Korea, 21 - 24 September (Abstract Accepted).

- Maulik M. Panseriya and Prof. Ashok K. Tiwari, ”Effect Of Blending Materials On Rheology Of Blended Cement” Thirteenth International Conference On Recent Advances In Concrete Technology and Sustainability Issues-2015, Committee for the Organization of International Conferences July 14-17, Ottawa, Canada.(Abstract Accepted)

- Maulik M. Panseriya and Prof. Ashok K. Tiwari, "Effect To Microfine Additives On Durability Of High Strength Concrete",Second International Congress on Durability of Concrete 2014, New Delhi, India.(Abstract Accepted).

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