CHAPTER 3

ADSORPTION STUDIES AND ZETA POTENTIAL MEASUREMENTS FOR DIFFERENT GRADES OF CEMENTS WITH SUPERPLASTICIZER

3.1 ADSORPTION STUDIES

3.1.1 Introduction

Superplasticizers are surface active agents with a high anionic charge (negative) which are attracted to the surface of the cement grain and are in sufficient numbers to get adsorbed and form a complete monolayer around the grain.

By virtue of the superplasticizers being adsorbed onto the cement grains, there is a physical separation (due to the like charges of the adsorbed superplasticizer molecules) and a rapid dispersion of the individual cement grains. By definition, adsorption denotes taking up of gas, vapour or liquid (adsorbate) by a surface or interface (adsorbent).

The adsorption of sulphonated melamine formaldehyde based superplasticizer, with different grades of cement, (namely grade 33, grade 43 and grade 53 cements) are first studied, to find out their dispersing capabilities on these cement grains. In addition their effect on the lignite fly ash obtained from Neyveli Lignite Corporation, Neyveli, is also investigated.
3.1.2 Literature Survey

The adsorption characteristics of superplasticizers on cement particles, their individual components and hydration products have been measured by many workers. Collepardi and co-workers (1981) have studied the adsorption of sulphonated napthalene formaldehyde condensates on cement particles using U-V absorption spectrophotometry.

Ramachandran (1983) had studied the adsorption behaviour of tri-calcium aluminate-gypsum water systems in the presence of superplasticizers.

Cunningham et al., (1989) studied the adsorption characteristics of sulphonated melamine formaldehyde condensates by high performance size exclusion chromatography. They have measured the average molecular weight and molecular weight distribution of sulphonated melamine formaldehyde condensate admixtures. They found that the molecules of higher molecular weight fraction get preferentially adsorbed onto the cement particles. Anderson and Roy (1987) of the Materials Research Laboratory in Pennsylvania, U.S.A studied the effects of adsorption of superplasticizers on the surface of cement using U-V adsorption techniques and micro electrophoresis. Different types of superplasticizers, namely, naphthalene, melamine and polystyrene were used with a single type of portland cement (Type 1). They conclude that polystyrene polymer should be a better dispersant than Melment, and this too should be a slightly better dispersion agent than sulphonated naphthalene formaldehyde.

3.1.3 Experimental Investigation by Adsorption Method

In our investigation, the superplasticizer of sulphonated melamine formaldehyde type (SMF), was a liquid and hence adsorption studies were done by measuring concentrations on dilution basis, rather than on weight
basis. Earlier research work done by Anderson *et al.*, and others used powder superplasticizers and dosed them on a weight basis for their adsorption studies.

**Ultra Violet Absorption Method:**

**Step I**

1. Different dilutions of the superplasticizer are prepared.
2. U-V spectrum is run and the peak is observed.
   - trial and error procedure is used.
   - once the peaks are got, in each case, the concentration of the solution and the peak absorbance value are noted.
3. A curve is drawn for different values of dilution Vs absorbance.

**Step II**

1. Cement/fly ash blends are mixed with superplasticizer and vortexed. The binding agent, namely cement/fly ash is separated from the solution by the following methods:
   a. Chromatograph column separation process run in a column using a fixed bed, that allows only the liquid to pass through.
   b. Centrifugation technique.
2. Filtered solution is now taken and the U-V spectrum is run.

**Step III**

1. Difference in concentration (as read from standard curve) is used as a measure of adsorption.

The first step in the experimental investigation involves the determination of U-V absorbance for various dilutions of the superplasticizer. This is done by a trial and error procedure, wherein the superplasticizer liquid
is diluted in steps of 1000X. 0.1 ml of the superplasticizer is taken and its volume is increased by adding distilled water 100 times (100X). This dilution is now thoroughly vortexed. 0.1 ml of this dilution (100X) is taken and the volume is again increased to 1000X. A U-V spectrum is run to measure the absorbance.

Basically, when an U-V radiation is incident on the superplasticizer liquid, the liquid is excited to a higher energy level, and when the frequency of the U-V radiation corresponds to the energy required to raise the system to a higher energy level in an allowed time interval, absorption occurs. The wave length at which the 'peak' of the spectrum occurs is read off on the X-axis and the 'absorbance' on the Y-axis, for a given liquid. Since, the U-V absorption varies with the concentration of the medium (in this case a superplasticizer liquid), the absorption spectra for various dilutions are run.

In our experiment, the minimum dilution of the superplasticizer liquid at which a peak was observed in the adsorption spectrum was 8000X. In this way, dilutions were prepared for 8000X, 10000X and 12000X and for each of these samples adsorption spectrum was found out. Once the dilutions are prepared and thoroughly vortexed, the samples are immediately transferred to the cuvette of the spectrometer. Since our investigation is based on dilution, any time delay would cause evaporation of water from the diluted sample and the results obtained will have some experimental errors.

The concentration of the melamine superplasticizer liquid was found out by U-V adsorption in the 190 nm - 400 nm band wavelength. A number of dilutions was performed in order to get a curve which had a peak. Dilutions were performed as follows: 0.1 ml of the liquid was taken using a pipette in a test tube. The volume was made upto 8 ml by adding distilled water. A 'PipetteMan' shown in Figure 3:1 with a disposable take up was used for accuracy. This solution which has a dilution of 80X is now vortexed for a
Figure 3.1 - Photograph - Pipette man
minute. Again 0.1 ml of this liquid is taken and the volume is made upto 10 ml, by adding distilled water, so that the dilution achieved is 8000 X.

\[(\text{ie}) \quad 0.1 \text{ ml of superplasticizer liquid (80 times)} \rightarrow 8 \text{ ml (80X)} \]
\[0.1 \text{ ml of 80X superplasticizer (100 times)} \rightarrow 10 \text{ ml (8000X)}.\]
The diluted liquid is then vortexed again for a minute.

This way, different dilutions are prepared in steps of 1000X. Each one of these samples are poured into the cuvette of the U-V spectrophotometer and the peak is observed. The following are the dilutions for which peaks are observed at a wavelength 215 nm:

<table>
<thead>
<tr>
<th>Concentration of the Liquid (SMF)</th>
<th>Wave Length nm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>12000X</td>
<td>215</td>
<td>1.816</td>
</tr>
<tr>
<td>10000X</td>
<td>215</td>
<td>2.099</td>
</tr>
<tr>
<td>8000X</td>
<td>215</td>
<td>3.286</td>
</tr>
</tbody>
</table>

Typical U-V absorption spectrum of melamine based superplasticizer is shown in Figure 3.2. A standard concentration run on anti-zero is now performed with the wavelength fixed at 215 nm and absorbance 0.430A. The following values are obtained in the standard concentration run:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance</th>
<th>Dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>12000X</td>
</tr>
<tr>
<td>2.</td>
<td>1.749</td>
<td>10000X</td>
</tr>
<tr>
<td>3.</td>
<td>2.110</td>
<td>8000X</td>
</tr>
<tr>
<td>4.</td>
<td>3.794</td>
<td></td>
</tr>
</tbody>
</table>

The standard curve is plotted with the values of concentration of the liquid on the X-axis and absorbance on Y-axis (Figure 3.3).
Figure 3.2 - Typical UV Spectrum of Melamine Based Superplasticizer
FIGURE 3.3 STANDARD CURVE PLOTED WITH THE VALUES OF CONCENTRATION AND ABSORBANCE
3.1.4 Adsorption Studies Using Chromatograph Column

When a superplasticizer liquid is mixed with a cement-water suspension, the superplasticizer molecules are adsorbed onto the surface of the cement grains. Once the solid (cement particles) and liquid phase (superplasticizer) is now separated, the concentration of the original liquid varies because of the adsorption process.

This phenomenon is made use of in an apparatus known as the 'chromatograph column' which is a separation process run in a column using a fixed bed, that allows the liquid to pass through while retaining the filter bed packing.

The chromatograph column used in the experimental investigation is shown in the photograph (Figure 3.4). The filter bed packing consists of finely divided sintered silica fused to the glass tube which tapers to a funnel portion below. Cement samples and fly ash wetted with water and mixed with superplasticizer are transferred onto the upper portion of the column. The liquid adsorbs first onto the samples of cement - fly ash and then filters down through into the conical flask.

Adsorption studies are now carried out for grade 33, grade 43 and grade 53 cements and fly ash. Adsorption of different grades of cement and fly ash by superplasticizer was effected by means of a liquid chromatograph column.

20 grams of grade 53 cement is taken and wetted with 8g of water in a conical flask. 90 ml sulphonated melamine formaldehyde superplasticizer is then taken and mixed with the cement paste in the conical flask immediately. The solution is then intimately mixed and vortexed for one minute on a vortex equipment (Figure 3.5). The contents are then emptied into the top portion of the filtration column and the same is allowed to filter
Figure 3.4 - Photograph - Chromatograph Column

Figure 3.5 - Photograph - Vortex Equipment
through the filtration bed. The bottom portion of the funnel of the filter is mounted onto a conical flask with a provision for connection to a vacuum chamber of the order of 400 mm of mercury. Thus, the bulk phase [that is the superplasticizer after adsorption] is collected from the conical flask. A dilution (10000X) is performed as explained earlier and the U-V spectrum of the superplasticizer liquid is obtained in the spectrometer after adsorption. The peak absorbance value, after a concentration run on anti-zero is found to be 2.564.

The same procedure as mentioned above is adopted for grade 43 and grade 33 cements respectively, and with fly ash. The absorbance values for the different cements and fly ash studied is shown in Table 3.1. Each of the values reported is the mean of six determinations, with a variance of 2% maximum. Fly ash cement combinations at 30% replacement of cement are also studied for adsorption.

<table>
<thead>
<tr>
<th>Items</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 53 Cement</td>
<td>2.050</td>
</tr>
<tr>
<td>Grade 43 + Fly Ash</td>
<td>1.749</td>
</tr>
<tr>
<td>Grade 33 Cement</td>
<td>1.601</td>
</tr>
<tr>
<td>Grade 43 Cement</td>
<td>1.509</td>
</tr>
<tr>
<td>Lignite Fly Ash</td>
<td>1.162</td>
</tr>
</tbody>
</table>

To have a cross-check on these values, the U-V spectrophotometer studies are repeated, but the adsorption was effected by means of centrifugation technique. That is, the mixture of cement paste and superplasticizer is first vortexed as in the above procedure through ultra-filtration. The contents are then placed in a centrifuging equipment and centrifuged for ten minutes. Solid-liquid separation (cements/fly ash from superplasticizer) is achieved and the liquid is now diluted again to 10000X. Absorbance values for two samples were found to give the same results as in the filtration technique.
The difference in concentration before and after adsorption for all the three cements, fly ash and fly ash-cement combination is read from the standard curve. Figure 3.6 shows the difference in concentration of the superplasticizer after adsorption with grade 33, grade 43 and grade 53 cements and lignite fly ash, in the form of bar chart.

3.1.5 Discussion on the results of Adsorption studies

It is observed from the figure that the percentage of superplasticizer adsorbed is maximum when fly ash alone is used as a solid. This is followed by grade 43 cement, grade 33 cement and then grade 53 cement.

That is, the adsorption of the superplasticizer (sulphonated melamine formaldehyde) is maximum for plain fly ash (lignite fly ash from Neyveli Lignite Corporation). Among cements adsorption is most on grade 43 cement followed by grade 33 cement. Adsorption is least (the difference in concentration before and after adsorption as measured by the U-V spectrum) for grade 53 cement. The adsorption of the superplasticizer is a maximum for grade 43 cement. However, when combined with fly ash (exactly with a 30% replacement of cement) it is found that the difference in concentration or the adsorption of the superplasticizer liquid is reduced. The individual adsorption characteristics of lignite fly ash alone show the maximum difference in concentration, that is, the maximum adsorption when compared to the three types of cements used.

From the bar chart, it is observed that melamine formaldehyde based superplasticizer is adsorbed least onto the grade 53 cement, as seen by the marginal difference in concentration before and after adsorption of the superplasticizer. Lignite fly ash used in this study shows the maximum adsorption onto the superplasticizer, indicated by the maximum difference in concentration of 13.8% before and after adsorption. Table 3.2 shows the difference in concentration, expressed as a percentage, for the different
FIGURE 3.6 DIFFERENCE IN CONCENTRATION OF SUPERPLASTICIZER ADSORBED BY VARIOUS CEMENTS & FLY ASH
cements and lignite fly ash. The initial concentration of the superplasticizer referred to is 1/10000.

Table 3.2 Percentage Difference in Concentration of Superplasticizer adsorbed for Cements and Lignite Fly Ash

<table>
<thead>
<tr>
<th>Items</th>
<th>% Adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 53 Cement</td>
<td>0.5%</td>
</tr>
<tr>
<td>Grade 33 Cement</td>
<td>9.0%</td>
</tr>
<tr>
<td>Grade 43 cement</td>
<td>12.0%</td>
</tr>
<tr>
<td>Lignite Fly Ash</td>
<td>13.8%</td>
</tr>
</tbody>
</table>

3.2 ZETA-POTENTIAL MEASUREMENTS

3.2.1 Introduction

Before the zeta potential measurements are described a very brief review of what zeta potential means, in connection with cement and superplasticizer liquid is given. As already mentioned superplasticizers are dispersing agents which possess an anionic charge. They are adsorbed onto the cement particles when mixed.

Consider a cement particle immersed in a superplasticizer liquid. Due to its high anionic charge the liquid superplasticizer molecules are strongly adsorbed onto the surface of the cement particle. Hence, there exists around the cement particle, a layer of rigidly held anionic charged liquid. This layer is known as the 'STERN LAYER' (Figure 3.7). The layer that separates this stern layer from the rest of the liquid is called the 'SHEAR PLANE'. That is, when an external electric field is applied, the liquid superplasticizer particles in the stern layer cannot be disturbed because of their strong adhesion (due to the opposite charge) to the cement particle. This adherence to the cement particle diminishes as the distance from the cement particle increases, and there exists a layer, which is not resistant to shear; that is when an external...
Figure 3.7 - Shear Plane (Stern Layer)
electric field is applied the liquid particles beyond this plane are relocated or can be disturbed. The potential that is measured at this plane when an external electric field is applied to a medium, (in this case to a cement-superplasticizer) is termed as 'Zeta-potential'. In general, when a potential gradient is applied across a colloidal suspension, the particles move toward the pole of opposite charge. The velocity of motion of particles is related to several factors, including their effective charge in motion, so that we must consider their potential at the plane of shear, that is their zeta potential (Figure 3.7).

3.2.2 Literature Survey

Nagele et al., (1985) in their paper 'Zeta potential of cement' have studied the zeta-potential of portland cement, blast furnace slag cement and fly ash. These have been measured at different initial pH values and the effect of an anionic surfactant is studied.

The following conclusions were drawn

Zeta-potential of cement and fly ash normally increases as pH increases due to higher concentrations in the stern layer. The zeta potential of blast furnace cement depends strongly upon the slag properties.

The zeta potential measurements of sulphonated melamine formaldehyde based superplasticizer with different grades of cement are first studied to find out the dispersing effect of this on these cements. In addition the effect on lignite fly ash - both when added alone and in a blended state was also investigated using the available facilities.
3.2.3 Experimental Investigation

The zeta potential measurements of sulphonated melamine formaldehyde based superplasticizer with different grades of cement are first studied to find out the dispersing effect of this on these cements. In addition the effect on lignite flyash - both acting alone and in a blended state was also investigated using the available facilities.

The mobility of the charged particles (termed electrophoretic mobility) can be determined in an arrangement where the velocity of a single particle is observed directly with a microscope. In our study a zeta meter is used to study the zeta potential of the three grades of cement and lignite flyash. The zeta potential was measured in a zeta meter manufactured by Rank Brothers Microelectrophoresis, Cambridge, England. A schematic diagram of the zeta meter is shown in Figure 3.8. The zetameter utilizes an electrophoretic technique wherein the material to be studied is placed in a liquid medium under a suitable electric field. As the particles move within the liquid medium towards the appropriate electrode, the velocity of migration is measured from which the zeta potential of the material is calculated according to the formula (taken from manual).

\[ \zeta = \frac{4\pi \times \eta T}{DT} \times EM \]

Where

- \( \eta T \) = viscosity of the suspending liquid, in poise at temperature \( T \).
- \( DT \) = dielectric constant of the suspending liquid at temperature \( T \).
- \( EM \) = electrophoretic mobility at actual temperature.
  - \( = \frac{x}{V.t} \)

Where

- \( x \) = distance travelled in \( \mu m \).
- \( V \) = applied voltage per 10 cm in volts.
- \( t \) = time in seconds.
Figure 3.8 - Photograph - Zetameter
The equation simplifies to

\[ \zeta = \frac{2.956 \times 10^3}{40 \times t} \text{ mV} \]

The electrophoresis cell is filled with the superplasticizer liquid (sulphonated melamine formaldehyde). 1 gram of cement is taken and wetted with water. It is then transferred to the cell containing the liquid. The electrodes are placed in position and a potential difference of 40 volt is applied between the electrodes.

The potential difference is chosen from trial and error. The potential difference applied, is chosen so that particle movement that it induces is neither too slow when seen in the field of the microscope, nor too fast. This makes tracking of the particle easy. The particle movement is viewed through the microscope, with the help of a powerful light source. The bottom layer of the cell is focussed and the mobility of the cement particles are tracked. Totally, seven particles were tracked in each case (for the different grades of cement and fly ash) and the average value of the time is taken. This is then substituted in the formula to get the zeta potential of the particles in the superplasticizer medium.

The following values of zeta potential were obtained:

- GRADE 43 CEMENT : -20.358 mV
- GRADE 33 CEMENT : -16.114 mV
- GRADE 53 CEMENT : -15.438 mV
- LIGNITE FLY ASH : -25.929 mV

The zeta-potential of lignite fly ash is a maximum in the superplasticizer medium compared to the cements. Grade 43 cement shows the maximum zeta potential followed by grade 33 cement and grade 53 cement. In simple terms, the dispersion of grade 43 cement is a maximum when mixed
with a sulphonated melamine formaldehyde liquid superplasticizer when compared to grade 33 and 53 cements.

3.3 DISCUSSION AND SUMMARY OF ZETA POTENTIAL RESULTS

The pattern of Zeta potential results exactly follows the observation made by adsorption studies. In zeta-potential studies too, the cement was blended with a lignite fly ash and the zeta-potential of the blended particles was observed. A 'Slowing down' of the particles were observed. The readings are not reported since it was not possible, with the instrument used, to find out which particle is being tracked; i.e., whether the reading taken is for the cement particle or for the fly ash particle. Hence, it is concluded from the zeta potential measurements of lignite fly ash and the different grades of cement that, the lignite fly ash is dispersed most when a superplasticizer is used. Among the cements, grade 43 cement is dispersed most, followed by grade 33 cement and lastly grade 53 cement.

It is to be noted that the combination of lignite fly ash and cement, causes a slowing down of the particles as viewed in the zeta-meter, which in effect means that the cements when blended with fly ash show a reduced dispersing tendency, when used in superplasticized concrete, as compared to the dispersing capabilities of lignite fly ash when used alone.

Thus, it can be concluded that, the dispersing action of the superplasticizer liquid is not increased when the two binding materials, namely, cement and fly ash are used in combination.