CHAPTER 3

METHODOLOGY

3.1 GENERAL

This chapter consists of two parts: a) the first part describes the materials and the geological protocols adopted and the second part b) discusses the engineering analytical methods following the flow chart (Figure 3.1).

Figure 3.1 Flow chart showing the methods adopted for the present study
3.2 Field Work

Volcanic ash samples were collected from the six different locations using the Global positioning system readings is shown in Figure 3.2 (Table 3.1). Fly ash samples were collected from the Ennore Thermal Power Station, Kathivakkam Village (15 Km North of Chennai). Samples of the volcanic ash, ash sediments and fly ash were collected using a shovel and collected in sample bags or zip lock plastic covers, marked and stored. The collected samples were then dried up to 50°C in the hot air oven and preserved for further analyses.

Table 3.1 Location of Volcanic ash in Andhra Pradesh

<table>
<thead>
<tr>
<th>Site Name</th>
<th>District</th>
<th>Latitude</th>
<th>Longitude</th>
<th>MSL (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ainavolu</td>
<td>Guntur</td>
<td>N 15° 32' 40.0''</td>
<td>E 79° 41' 44.9''</td>
<td>72</td>
</tr>
<tr>
<td>Jwalapuram</td>
<td>Kurnool</td>
<td>N 15° 19' 18.6''</td>
<td>E 78° 07' 55.3''</td>
<td>250</td>
</tr>
<tr>
<td>Kalasapadu</td>
<td>Cuddapah</td>
<td>N 15° 06' 43.8''</td>
<td>E 78° 56' 09.6''</td>
<td>218</td>
</tr>
<tr>
<td>Porumamilla</td>
<td>Cuddapah</td>
<td>N 15° 00' 10.0''</td>
<td>E 78° 59' 45.0''</td>
<td>190</td>
</tr>
<tr>
<td>Singampalli</td>
<td>Cuddapah</td>
<td>N 15° 13' 32.3''</td>
<td>E 78° 53' 34.1''</td>
<td>232</td>
</tr>
<tr>
<td>Vankamari</td>
<td>Cuddapah</td>
<td>N 14° 56' 12.0''</td>
<td>E 78° 56' 36.3''</td>
<td>146</td>
</tr>
</tbody>
</table>

Figure 3.2 Volcanic ash sites explored in Cuddapah basin
3.3 GEOLOGICAL PARAMETERS

3.3.1 Textural Analysis

3.3.1.1 Sand, silt and clay ratio

For conducting the various analyses, ash samples were initially cone and quartered to ensure uniformity and avoid sampling errors. The ash samples were analyzed for textural composition using the pipette method following the protocols put forward by Krumbein & Pettijohn (1938).

![Figure 3.3 Sand, silt and clay ratio of volcanic ash and fly ash](image)

5 grams of the air dried ash sample was mixed with a pinch of Sodium Hexa Meta-phosphate as a dispersal agent with approximately 250 ml of water and stirred allowed to stand for 15 minutes. The sample was then collected in the #230 ASTM mesh (63 µm), and washed with deionised water,
dried, weighed and the sand percentage was calculated. The particles below the 63 µm were collected in the sieve pan and were then poured into a 1000 ml beaker, thoroughly mixed with deionised water for uniform distribution (Figure 3.3). 20 ml of the sample solution was then pipetted out into a beaker from the jar at 123 minutes following Carver (1971) to measure the clay size particles. The beaker was dried, weighed and measured for the clay size particles and its percentage was calculated. Silt percent was calculated by subtracting the sand and clay values. The grain size variations were plotted in a ternary diagram following Sheppard (1954) for further grain size and textural interpretations.

3.3.1.2 Mechanical sieve

Sediment dominant with coarser particles were measured using mechanical sieve analysis, following the method given by Carver (1971). 100 grams of the sediment sample were first treated with mild Acetic acid (0.5 M) to remove the carbonate coatings and further treated with H₂O₂ to remove the organic matter. The sediments were then washed with deionised water and dried then sieved using an automatic electrical Roe tap sieve shaker with ASTM mesh sizes no #18, #25, #35, #45, #60, #80, #120, #170 and #230 for 10 minutes (Figure 3.4). The sediments retained in each sieve size were then measured and calculated for weight percentage. Cumulative plots were then plotted for inferring grain size, textural characters and processes of deposition. Statistical parameters like graphical mean, graphical standard deviation, graphical skewness, and graphical kurtosis were computed to process sediment textural characteristics following (Folk & Ward 1957).
3.3.2 Laser Diffraction

The grain size fraction of the volcanic ash sediments and thermal ash dominant with fine materials were measured using Laser diffraction technique, (Mastersizer 2000), user manual, Malvern Instrument 2007 (Figure 3.5), in the Department of Geology, Anna University. The Laser diffraction device can measure the particle size from 0–1000 µm and in this study an average of three analyses per sample is presented. Sand, silt and clay were plotted using a ternary diagram following Unified Soil Development Agriculture Soil texture classification.
3.3.3 Major Oxides

The ash samples were analysed for their geochemistry. X-ray Fluorescence (XRF) instrument was used for its high accuracy and application of repeated analyses on the non-destructive samples (Wien et al 2005). Major oxide analysis of the ash samples was analyzed using the Bruker S4 – Pioneer XRF spectrometer following the powder method. The XRF analyses were carried out at the Central Instrument Facility, Pondicherry University (Figure 3.6).
For this purpose, 5 grams of the ash samples were crushed using agate mortar and ground to less than #230 ASTM meshes (63 μm). These samples were pre-treated with 1N HCl to remove the carbonate content from the sediments, the residue (other than carbonate) was then washed several times using deionised water, dried and further powdered to ascertain the grain size less than 230 ASTM mesh (63 μm) in a clean, uncontaminated agate mortar and then riffle split to homogenize the powdered samples. The powdered samples were then pressed with high pressure to make pellets of equal density following Grieken & Markowicz (2002). These samples were further analysed for the major oxides such as SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, Na₂O and K₂O. The average errors for the major oxides analysed were less than ± 5 %. Standard values of the Upper Continental Crust (UCC) were adopted for comparison (Table 3.2).
Table 3.2 Standard values for major and trace elements

<table>
<thead>
<tr>
<th>Element</th>
<th>UCC %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>66</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5</td>
</tr>
<tr>
<td>MnO</td>
<td>0.08</td>
</tr>
<tr>
<td>MgO</td>
<td>2.2</td>
</tr>
<tr>
<td>CaO</td>
<td>4.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.9</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.4</td>
</tr>
</tbody>
</table>

The scanning electron microscope (SEM) instrument was used to determine the surface morphological characteristics of the ash samples with enhanced resolution. The morphological studies were examined using Hitachi.
3.4 POZZOLANIC CHARACTERISATION

In the present study, Pozzolanic characterization involving the degree of pozzolanic reaction between the reactive silica and consumption of calcium hydroxide can be quantified using X-Ray Diffraction spectra. In the case of lime saturated test the consumption of calcium hydroxide is determined using direct chemical analysis.

3.4.1 X–Ray Diffraction

X–Ray powder diffraction (XRD) method was adopted to determine the mineralogy and crystalline phase of the ash samples. The procedure was carried out using the Bruker D2 Phazer (Germany) diffractometer instrument equipped with Cu-K\(\alpha\) radiation using X-ray powder diffraction (XRD, Bruker D8 Advance diffractometer, with Cu K\(\alpha\) radiation in the range of 10°- 70° 2\(\theta\), (with steps of 0.02°/ Sec) at the Department of Physics, Anna University Chennai, following Moore & Reynolds (1997) (Figure 3.8).

![Figure 3.8 X–Ray Diffraction Instrument](image-url)
3.4.2 Lime Saturation Test

The lime saturation test is a direct chemical titration method to determine the pozzolanic characteristics of the material. In this method, a controlled quantity of lime is added at the beginning of the test and the residual lime in solution is measured later, which explains the pozzolanic reaction of the material with respect to time (Donatello 2010). For the lime saturation test; ash samples were prepared adding 1 g of volcanic ash to a plastic container containing 75 ml of saturated lime solution (Figure 3.9 A). The saturated lime solution was prepared by dissolving 2 g of hydrated lime in 1 litre of distilled water. The bottles were then sealed and placed in an oven at 40 ºC for 1, 3, and 7 days.

![Figure 3.9 Lime saturation test (A) Material added (Lime & volcanic ash) (B) Buckner funnel and plastic container (C) Initial point wine red (D) End point steel blue](image-url)
The solution was separated by filtering the mixed sample with 2.7 µm vacuum filter paper (Whatman No. 542) above a Buchner funnel (Figure 3.9 B) and sealed. The 50 ml of filtrate solution was then titrated against 0.03 mol / l EDTA solution using the Erichrome Blank T indicator. Initially, after adding the indicator the solution became red wine in colour (Figure 3.9 C). EDTA solution was slowly, then added from the burette to the beaker and gently swirled till the colour changed to steel blue (Figure 3.10 D). The results of this titration were reported as a percentage of the total CaO fixed per gram of test pozzolan with respect to time (1, 3, and 7 days).

3.5 APPLICATION IN BUILDING MATERIALS

3.5.1 Hand Mould Brick

The process for manufacturing hand mould brick required volcanic ash samples as the main component; additional materials included OPC grade 53, and sand (graded zone). The moulds were rectangular wooden boxes, which were open at the top and bottom of the mould. Initially, fine sand and cement were first placed in a mixer and dry mixed (Figure 3.10 A). The volcanic ash sample was then added and mixed in the above mixture (Figure 3.10 B). The mixer was kept covered with burlap during the mixing to avoid the volatility of the materials. Water with 0.5 w/c ratio was then added to the constituent materials and mixed thoroughly over and over to make as uniform (Figure 3.10 C).

The material was mixed well till it become homogenous and then placed and well compacted in a mould with dimension 230 X 110 X 70 mm³ at room temperature 25 ± 2° C. The brick was removed from the mould after 24 hours (Figure 3.10 D). The brick samples are cured with water at room temperature for 7th day and 28th day of the test. Three bricks were used in each compressive strength test and the average value was taken on the 7th and
28th day using a universal testing machine (Figure 3.10 E). The water absorption of the bricks was done after a curing period on the 28th day. Compressive strength and water absorption were conducted in the Department of Structural Engineering, Anna University, Chennai as given in IS 3495 (part I): 1992; IS 3495 (part II): 1992.

![Preparation of brick specimen](image)

**Figure 3.10** Preparation of brick specimen, A. Mixture of ash with sand, B. Additional mixture of cement, C. Addition of water, D. Brick sample after curing, E. Test sample placed in the universal testing machine

### 3.5.2 Portland Pozzolan Cement

#### 3.5.2.1 Strength activity index

The pozzolanic performance of blended cement was evaluated using strength activity index test, where the volcanic ash sample of volcanic
ash acted as a blended specimen. The specimen of control and reference mixture was prepared as per the American standard “ASTM C311”. The material used for the preparation of mortar was OPC cement (53 grades), volcanic ash and graded sand as per Indian Standard “IS 383” (Figure 3.11 A). The material was mixed (Control and 20% volcanic ash blended) in a planetary orbital mixer for 5 minutes with necessary water (Figure 3.11 B). For casting the material, six glass mould cubes of 5 cm size in dimension were prepared (Figure 3.11 C). Before casting the material, the water flow value of the mixed material (Control and 20% volcanic ash blended) was verified as per the standard ASTM C 1437 – 07 (Figure 3.11 D). The casting sequence was followed as per Figure 3.12 for both control and reference mortar and its strength were determined for 7th day and 28th day of curing. A total of six mortars were separately prepared for the control specimen and the volcanic ash blended specimen (Table 3.3).

<table>
<thead>
<tr>
<th>Mortar</th>
<th>Control</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC Cement (g)</td>
<td>500</td>
<td>400</td>
</tr>
<tr>
<td>Volcanic ash (g)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Standard sand (g)</td>
<td>1375</td>
<td>1375</td>
</tr>
</tbody>
</table>

The water added to the replacement mortar will differ with the control mortar (242 ml). This can be found using trial and error method of the flow test (Figure 3.12 A). The material was then mixed well and compacted in a mould at room temperature 23 ± 2° C (Figure 3.12 B). The cubes were demolded after 24 hours and then immersed in water saturated with lime until the testing age (Figure 3.12 C). Each cube with the requisite age was tested.
for compression using a universal testing machine (Figure 3.12 D). The Strength Activity Index (SAI) was calculated as follows.

\[
\text{SAI} \% = \left( \frac{\text{Compressive strength of reference mortar (20% volcanic ash)}}{\text{compressive strength of control mortar}} \right) \times 100.
\]

**Figure 3.11** Casting of material (A) Material – OPC cement, volcanic ash and Standard Sand (B) Mixing of material with water (C) Flow test (D) six glass moulds with 5cm cube.
3.5.2.2 Frattini Test

The Frattini test is a direct method of determining the pozzolanic activity that involves chemical titration to determine the calcium hydroxide consumption by monitoring concentration of dissolved $[\text{Ca}^{2+}]$ and $[\text{OH}^-]$ concentrations in a solution containing OPC 53 and the test pozzolan. In the present study, the Frattini test was conducted following the British standard EN 196-5. The sample were prepared by mixing 16 g of OPC 53 and 4 g of volcanic ash samples were mixed with 100 ml of boiled water and then
shaking them rigorously for 20 seconds (to avoid formation of cement lumps) in a plastic bottle. Afterwards, the samples were sealed and stored for 8 days and 15 days at 40 °C. Later the solution was separated within 30 seconds (to avoid absorption of atmospheric carbon dioxide) by using a 2.7 µm vacuum filter paper (Whatman No. 542) above the Buckner funnel and sealed similar to the procedure followed in lime saturation test (Figure 3.9 A & B). [OH⁻] and [Ca²⁺] analysis were carried out after 8 days and if the test results satisfied the pozzolan character of the sample then the same test was not carried out after 15 days.

To determine the hydroxyl ion, 50 ml of filtrate solution was pipetted out in a beaker. 5 drops of methyl orange indicator were added to it and titrated against dilute 0.01 mol/l dilute hydrochloric acid. Initially the solution in the beaker was yellow (Figure 3.13 A). After diluting, HCL solution was added from the burette to the beaker and swirled gently. Eventually the solution changed from yellow to orange and the reading was noted (Figure 3.13 B). To determine the calcium oxide titration of the same sample solution against 0.03 mol/l EDTA solution with a pH of 12.5 was carried out. Initially, the solution was titrated against dil. HCL, so the solution was acidic in nature with pH less than 7. The pH was increased by adding an alkaline solution. (Figure 3.13 C). Further Patton and Readers reagent was added to the solution as an indicator and titrated against EDTA solution. Initially, the solution in the beaker was purple in colour (Figure 3.13 D), and then on adding EDTA solution from the burette to the beaker and swirled gently the mixture changed colour from purple to blue colour and the reading was noted (Figure 3.13 E). The results are presented as an isotherm curve or saturated curve of [Ca²⁺], expressed as equivalent CaO, in mmol/l versus [OH⁻] in mmol/l. Test results lying below the saturated curve indicated
pozzolanic activity and if the results were above the curve the tested samples represented having no pozzolanic activity.

Figure 3.13 Frattini test (A) titrating the solution with initial colour yellow (B) end point as orange (C) pH adjustment in solution (12.5) (D) Initial point purple (E) End point blue.