

CHAPTER 3

METHODOLOGY

This chapter presents the specifications of the materials used in the experimental program and the preliminary tests conducted on the materials. The mix proportion adopted for synthesising the geopolymer with details on mixing, casting and curing process are also presented. At the end, a flow chart depicting the steps involved in carrying out this study is presented.

3.1 Materials

The constituents of geopolymer concrete are aluminosilicate raw material (Flyash or metakaolin), Sodium silicate solution and Sodium Hydroxide solution together called alkaline activator solution, fine and coarse aggregates. Aluminosilicate raw material reacts with the alkaline activator to form sodium aluminosilicate gel which surrounds the aggregates and hardens into a rock-like mass.

3.1.1 Flyash

Flyash is a by-product of combustion of coal, fired in thermal power stations. Type of flyash generated depends on the coal fired. Generally, bituminous coal generates low calcium Flyash (class F) and sub-bituminous and lignite coal generates High calcium Flyash (Class C). Class F fly ash is pozzolanic and non-cementitious. Class C flyash is pozzolanic and cementitious. The specific gravity of Class C flyash is little higher at 2.5 - 2.8 compared to Class F flyash at 2.2 -2.5. In this research work, low calcium flyash class F is used and is procured from Ennore thermal power station located in Chennai, TamilNadu, India. It conforms to ASTM C 618 class F

pozzolan and IS 3812-1981, Specification for flyash for use as pozzolan and admixture and is presented in Table 3.1

Table 3.1 Conformation of Flyash Specification to Standards

Compound	ASTM C618 Class F Specification in %	IS 3812 Specification in %	Actual Composition in %
CaO	< 5	-	1.76
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃	>70	>70	89.7
SO ₃	<5	<2.75	0.5
Na ₂ O	<1.5	<1.5	0.39
Loss on ignition	<6	<12	1.61
SiO ₂	-	>35	48
MgO	-	< 5	0.89

Flyash particles are spherical in shape and help in blending with other materials. The particle size of flyash is as high as D75 is 45µm.

3.1.2 Metakaolin

The composition of metakaolin depends on the composition of Kaolin clay used for calcination. The heating temperature, timing and rate of heating as well as cooling rate and temperature significantly affect the dehydroxylation process. Prolonged heating exceeding 800 °C reduces the pozzolanic property. Metakaolin of three different compositions have been used in this study conforms to ASTM C 618 class N pozzolan and IS 1344-1981 Specifications for calcined clay pozzolan and the details are presented in Table 3.2.

Table 3.2 Conformation of Metakaolin Specification to Standards

Compound	ASTM C 618 Class N Specification in %	IS 1344 Specification in %	Actual Composition in %
CaO	<1	< 10	0.29
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃	>70	>70	96.41
SO ₃	<4	<3	Nil
Na ₂ O+K ₂ O	<1	<3	0.49
loss on ignition	<10	<10	1.00
SiO ₂	-	>40	52
MgO	-	< 3	0.2

In this study, metakaolin of three varied compositions (M1, M2, M3) is used for geopolymer synthesis. M1, M2, M3 precursors satisfy the requirements of IS 1344-1981, Specification for calcined clay pozzolan. Mass of SiO₂+Al₂O₃+Fe₂O₃ should not be less than 70%, SiO₂ not less than 40%, and a fineness not less than 250-320 m² /Kg. The specific gravity of M1, M2, M3 are 26.06%, 24.27% and 21.35% higher compared to FA, that would result in a slightly heavier material. The specific gravity of M3 is less compared to M1 and M2 suggest that the particle size of M3 is less compared to M1 and M2. The particle size of M1, M2, and M3 as given by manufacturers are given in Table 3.3. Loss on ignition of flyash is >1 is indicative of the presence of unburnt coal particle.

Table 3.3 Chemical composition of M1, M2, M3 and FA

Chemical (%mass)	Metakaolin 1	Metakaolin 2	Metakaolin 3	Flyash
SiO ₂	52.0	56.86	58.90	48.0
Al ₂ O ₃	46.0	40.10	37.23	29.0
Fe ₂ O ₃	0.60	0.45	1.70	12.7
TiO ₂	0.65	0.36	0.42	-
CaO	0.09	0.28	0.29	1.76
MgO	0.03	0.20	0.20	0.89
Na ₂ O	0.10	0.25	0.23	0.39
K ₂ O	0.03	0.20	0.26	0.55
SO ₃	-	-	-	0.5
Loss on ignition	1.00	1.0	< 1	1.61
Physical property				
Specific gravity	2.6	2.56	2.5	2.06
Specific surface area m ² /g	19-20	19-20	19-20	10.5

Details of particle size and bulk density of Metakaolins M1, M2, M3 are given in Table 3.4 as given by the manufacturers. While M1 contains particles above 44 µm upto 3% by mass giving rise to a bulk density of 400-500 g/litre. The bulk density of M3 clearly indicates that it is finer than M1 and M2. .

Table 3.4 Particle Size of Flyash and Metakaolin

Material	Particle size	Bulk density
M1	>44 μm -3% max <2 μm - 50% min	400-500 g/litre
M2	>25 μm -0.05%	500 g/ litre
M3	>45 μm -0.05%	270-330 g/litre

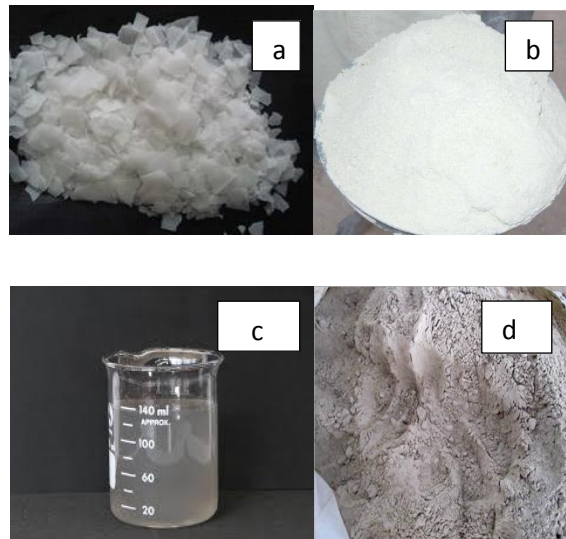
3.1.3 Fine aggregate

Aggregates constitute around 70-75% of the mass of concrete. They are distinctly classified as one finer than IS 4.75 mm sieve and the other coarser than 4.75 mm IS sieve. Coarse and fine aggregates used for cement concrete are suitable for geopolymer concrete.

Aggregates used in this study are natural sand and crushed granite conforming to IS 383- Specifications for coarse and fine aggregates from natural sources for concrete. They should be free from any adherent coating, vegetable matter, alkali and any deleterious substances. Elongated and flaky aggregates are less preferred compared to cubical shape. Aggregates that are chemically reactive with binder will affect the strength of concrete. The fine aggregate used in this study conforms to Zone 2 is illustrated in the sieve analysis presented in Table 3.5 with a fineness modulus of 2.73. Aggregates are tested according to IS 2386-1963, Specifications for Methods of tests for aggregates for concrete.

Table 3.5 Sieve Analysis of Fine Aggregate

IS Sieve	Cumulative Weight Retained(g)	Cumulative % Retained	Cumulative % passing	IS 383 Zone II %
4.75 mm	74	7.4	92.6	90-100
2.36 mm	194	19.4	80.6	60-95
1.18 mm	559	55.9	44.1	30-70
600 μ	705	70.5	29.5	15-34
300 μ	787	78.7	21.3	5-20
150 μ	942	94.2	5.8	0-10
Lower than 150 μ	1000	-		



- a) NaOH flakes b) Metakaolin
 c) Sodium Silicate d) Flyash
 Solution

Figure 3.1 Geopolymer Constituents

3.1.4 Coarse Aggregate

Coarse aggregates must possess good crushing strength, interlocking property and low water absorption. Sieve analysis results are presented in Table 3.6.

Table 3.6 Sieve Analysis of Coarse Aggregate

IS Sieve	Weight Retained (g)	Cumulative Weight Retained	Cumulative % Retained	Cumulative % passing	IS 383 specification %
80 mm	0	0	0	100	-
40 mm	0	0	0	100	-
20 mm	63	63	3.15	96.85	95-100
10 mm	1400	1463	70.00	30.0	25-55
4.75mm	524	1987	99.35	0.45	0-10
2.36mm	0	2000	100	0	-
1.18mm	0	2000	100	0	-
600 μ	0	2000	100	0	-

3.1.5 Alkaline activator

The two constituents of alkaline activator are NaOH and Sodium silicate solutions. The common name for NaOH is caustic soda. While handling NaOH, proper protection is to be taken, as it may cause mild skin irritation. NaOH flakes of 99% purity are used in this study. NaOH flakes are hygroscopic and not to be exposed to air. When exposed to air it absorbs moisture and gradually liquefies. It absorbs CO₂ from the air and in the presence of minimal moisture forms Sodium bicarbonate and loses its strength. NaOH flakes, when dissolved in water, gets ionised into Na⁺ and OH⁻ ions. Excess of OH⁻ ions makes the solution alkaline.



10 M NaOH solution used in this study is prepared by dissolving 400 grams of NaOH flakes in one litre of distilled water. Distilled water is preferred to avoid impurities in dissolution.

Na_2SiO_3 solution acts as a catalyst in geopolymer synthesis. Two grades of sodium silicate solutions available are alkaline and neutral. Neutral solutions are used in pharmaceutical and adhesive industries. Alkaline solutions are used in detergents, paper, cement and textile industries. Na_2SiO_3 solution is viscid and translucent with pale white or grey colour. Sodium Silicate solution conforming to IS 381(1995) Indian Standard sodium silicate –Specification is used in this study having Na_2O (8.74 %), SiO_2 (27.96%), H_2O (63.3%) with the modulus of 3.2 (mass of $\text{Na}_2\text{O}/\text{SiO}_2=3.2$) is used. Figure 3.1 shows the pictorial representation of geopolymer constituents.

3.2 Preliminary Laboratory Investigations

3.2.1 Specific Gravity

Specific Gravity of fine and coarse aggregates are found using pycnometer and water. Specific Gravity of Flyash and Metakaolin is found using Kerosene in Le Chartier flask. Specific Gravity values are tabulated in Table 3.7. The setup used for the determination of Specific Gravity is given in Figure 3.2

Table 3.7 Determination of Specific Gravity

Material	Specific Gravity
Fine aggregate	2.7
Coarse aggregate	2.76
Flyash	2.06
Metakaolin	2.6

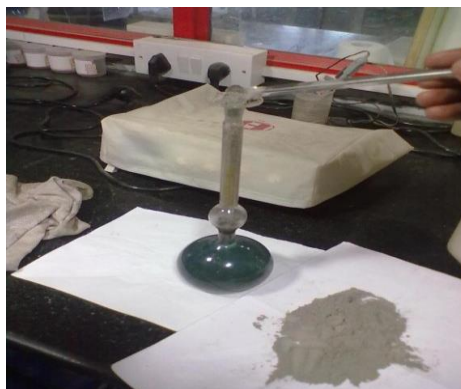


Figure 3.2 Le Chatelier flask to determine Specific Gravity

3.2.2 Fourier Transform Infra -Red Spectroscopy

Infra-Red spectroscopy is an important analytical technique available for gathering information about the material at the molecular level. Infrared radiation is passed through a sample and these radiations are absorbed at a particular energy. Infra- red spectrum originates from the vibrational motion of the molecule. Vibrational frequencies are the energy signatures of the compounds. The percentage of energy absorbed (A) is plotted against the wave number (cm^{-1}) at which absorption occurs to have Infrared spectrum. This is a versatile technique in which any sample in any condition can be studied.

This analytical technique has greatly improved with the advent of FTIR spectroscopy, and the time involved has reduced. FTIR spectroscopy uses an interferometer to produce a spectrum and a mathematical technique of Fourier transform to obtain the final spectrum. Absorption and transmittance are two techniques followed in FTIR spectroscopy. Stretching and bending vibrations of the atoms in a molecule can also be identified.

Perkin Elmer spectrum 10.4.2 FTIR spectrometer is used for obtaining the FTIR spectrum of Metakaolin 1 sample. It consists of globar and mercury vapour lamp as sources of interferometer chamber followed by a sample chamber and a detector. The entire region of 4000 cm^{-1} to 450 cm^{-1} is covered in this instrument. Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest. It has a typical resolution of 0.5 cm^{-1} . Spectral manipulations like signal averaging, signal enhancement and base line corrections are possible.

FTIR spectrum for Metakaolin 1 sample is presented in Figure 3.3. The absence of a peak at $3800\text{-}3200\text{ cm}^{-1}$ and $1700\text{-}1600\text{ cm}^{-1}$ confirms that there is no O-H bond in stretching vibration and bending vibrations respectively. This implies that the calcination of kaolin is complete and no water is present in metakaolin. Other significant bands present in the sample as read from the spectrum is presented in Table 3.8.

Table 3.8 FT-IR Spectrum Vibrational Band Assignment of Metakaolin

Frequency cm^{-1}		Vibrational band assignment
FTIR	Intensity	
827	Strong	Al-O asymmetric stretching
734	Strong	Al-O symmetric stretching
554	Very strong	Al-O Bending
887	Weak	Si-O symmetric stretching
1088	Very strong	Si-O asymmetric stretching

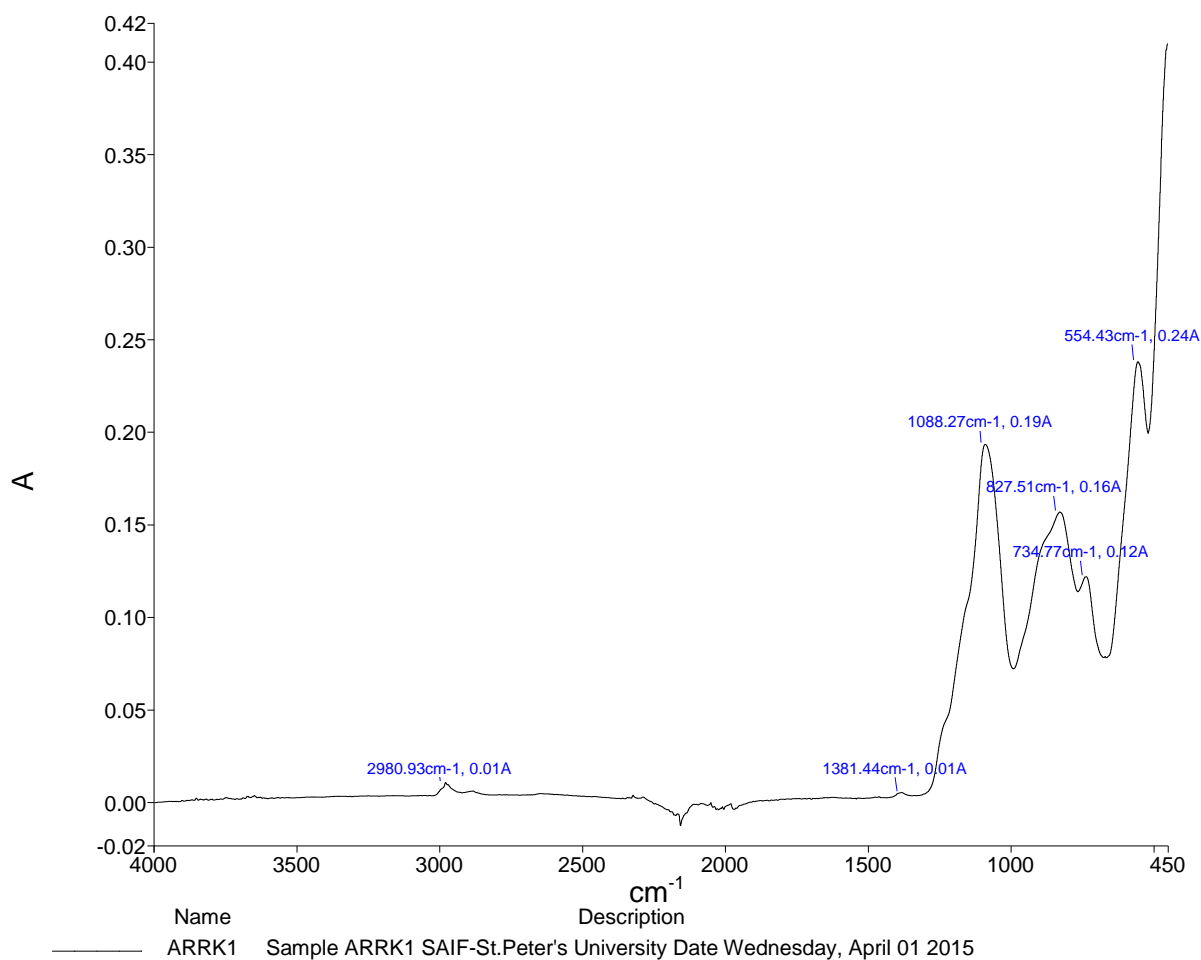


Figure 3.3 FT-IR Spectrum of Metakaolin 1

FTIR spectroscopy investigation for metakaolin 1 sample has been done in Sophisticated Analytical Instrumentation Facility (SAIF) present in St. Peter's University, Chennai.

3.2.3 SEM Analysis

The first step of a scientific evaluation is to thoroughly observe the form of the material. For this purpose, a magnifying glass or an optical microscope can be used. But, as long as light is used, anything smaller than the wavelength of light (400-700 nm) cannot be seen and therefore observing a Nanostructure is extremely difficult.

The Scanning Electron Microscope (SEM) utilises an electron beam whose wavelength is shorter than that of light, thereby enabling the observation of a structure down to several nm in scale. Scanning electron microscope uses an electron beam which is directed towards the specimen under examination. An electronic gun located on the top of the device shoots out a beam of highly concentrated electrons. There are two main types of electronic guns. The first, thermionic guns, heat a filament until electrons stream away. The second, field emission guns rip electrons away from their atoms by generating a strong electrical field. The microscope composed of a series of lenses within a vacuum chamber. These lenses direct the electrons towards the specimen in order to maximise efficiency. When more electrons are used, the more powerful is the magnification. When a specimen is hit with a beam of the electrons known as the incident beam, it emits X-rays and three kinds of electrons; Primary backscattered electrons, secondary electrons and auger electrons. The SEM uses primary backscatter electrons and secondary electrons.

An electronic recorder picks up the rebounding electrons and records their input. This information is translated onto a screen which allows three-dimensional images for clear representations. The SEM's greatest advantage is its ability to produce textual information in a consistent and coherent manner.

Traditional SEM was not able to produce colour images, as the electrons merely revealed information about the sample size and topography. However, recent advances have enabled measurement of energy signatures by researchers in the samples reaction to the incident beam impact. These energy signatures are then colour coded, with each different element, producing its own specific signature. By referring to these colours, scientists can identify, in extreme detail, the borders of each element.

The process can work only if the sample is properly prepared. Metals require no preparation, as they already have ability to conduct electricity and respond favourably when bombarded with electrons. However, non-metals need to be prepared with a material known as a sputter coater. Sputter coater provides the specimen with a thin layer of conductive material, usually Gold which is acquired through the use of an electric field and an argon gas. The electric field dislodges an electron from the argon, resulting positively charged ions. These positive ions are then attracted to gold foil, which is negatively charged. As they settle onto the gold, the argon ions expel gold atoms, which fall onto the specimen, covering it with a thin conductive coating.

In addition, preparation traditionally includes the removal of all water. Water molecules vaporise in a vacuum, creating obstacles for electron beams and obscuring the clarity of the image. However, a number of newer SEMs no longer require a full vacuum to operate. These devices produce images at weaker resolution, but they open up the possibility of examining a whole range of previously untouchable sample, crucial for a number of different industries and discipline.

SEM uses energy dispersive X-ray spectroscopy in the production of elemental maps, which accurately represent the distribution of elements within samples. The most typical uses are elemental analysis, mineral orientation, morphology and contrasts. While the SEM has surpassed in power by newer microscopes, it remains highly useful on the market, as few others can operate with a similar broad range of samples. Today, researchers all over the world rely on SEM for accurate visual information. Figure 3.4 clearly gives the difference in particle morphology of flyash and Metakaolin particles. Flyash particles are spherical in shape whereas Metakaolin particles have flat plate-like shape giving rise to higher specific area to react.

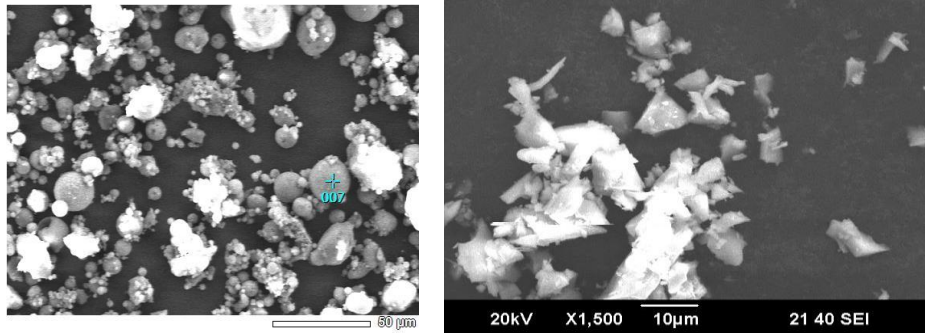


Figure 3.4 SEM image showing particle morphology of flyash and Metakaolin

SEM and EDS analyses are carried out in the analytical facility present in Corporate Technology centre, Tube Investments of India Limited, Avadi, Chennai. JEOL JED 2300 Analysis station is used for SEM and EDS analysis in this study and an image of this equipment is presented in Figure 3.5. The JED-2300 Analysis Station is an element analysis system offering seamless observation and analysis. The EDS analysis can be launched by designating the spot directly on the SEM image. By comparing the collected X-ray spectrum to the synthesised spectrum created using the visual peak ID (VID), quantitative results can be analysed both visually and numerically.



Figure 3.5 JEOL JED 2300 Analysis station

In the element map collected with the JEOL EDS, the spectrum is saved in the pixels of each frame. The images generated by the electron beam are also stored for each frame. The playback function provides diverse analysis options, including the observation of the spectrum changes over time. Replay of the data after measurement is completed is also possible, enabling the previously impossible observation of the process of the specimen change over time. Playback also supports extraction of the desired frames.

3.2.4 EDS Analysis

Energy-dispersive spectroscopy (EDS), sometimes called energy dispersive is an analytical technique used for the elemental composition or chemical characterization of a sample. Each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum. A high-energy beam of charged particles such as electrons is focused into the sample being studied for stimulating the emission of characteristic X-

rays from a specimen. At rest, an atom within the sample contains unexcited state electrons in discrete energy levels bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron-hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and the volume of energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows measurement of the elemental composition of the specimen. Figure 3.6 depicts the powder samples of flyash and Metakaolin blown onto the carbon tape ready for analysis.

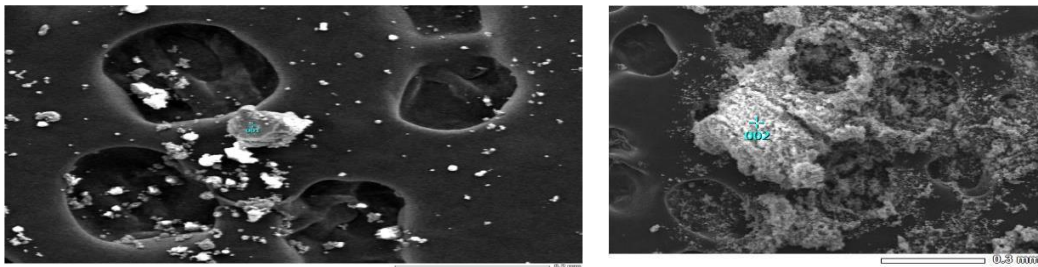


Figure 3.6 EDS image of flyash and Metakaolin on carbon tape

The powder samples should be blown onto a carbon tape and sputter-coated with platinum for fixing the particles in place and to improve conductivity as the samples are non-conductive. The holes like features found in Figure 3.6 are on the carbon tape. When the electron beam interacts with the electrons in the atoms, some electrons from the atoms in the sample are ejected and an X-ray with characteristic energy of the element is emitted (depending on the electron arrangement in the atomic orbitals which is unique to each atom). These characteristic X rays are used for identifying the chemical composition of the sample. The major constituents of flyash are elements of Si and Al at 24.6

percentage and 13.96 percentage by mass followed by elements of Fe and Ca at 16.74 by mass by EDS analysis. The presence of other elemental masses in flyash is given in Table 3.9.

Table 3.9 EDS Analysis for flyash

Element	keV	Mass (%)	Counts	Error (%)	Atom (%)	Cation K
O K	0.525	11.85	2722.37	0.01	24.09	1.3028
Mg K	1.253	2.93	929.51	0.09	3.92	0.9446
Al K	1.486	13.96	4241.90	0.02	16.83	0.9854
Si K* (Ref.)	1.739	24.60	7362.32	0.01	28.49	1.0000
Ca K	3.690	16.74	3210.01	0.03	13.59	1.5611
Ti K	4.508	2.21	332.97	0.29	1.50	1.9909
Fe K	6.398	16.74	1633.37	0.06	9.75	3.0674
Pt M*	2.048	10.96	799.19	0.15	1.83	4.1054
Total		100.00			100.00	

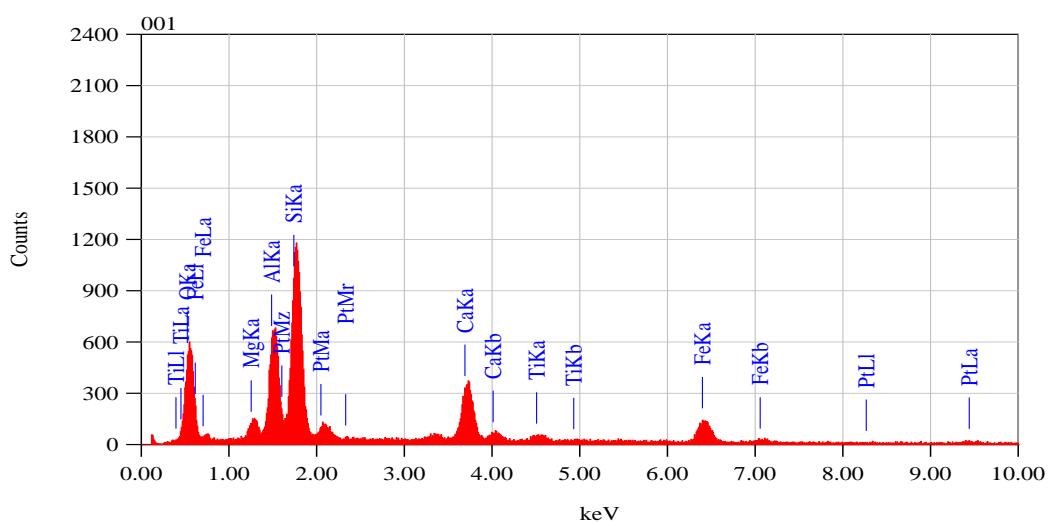


Figure 3.7 EDS analysis for flyash (Si/Al = 1.762)

The standardless method refers to the technique of storing data on characteristic energy emission from elements in the system used for analysis and using it for quantification of the elements. Ka, Kb, La, L1, as representative of the energy emitted by electrons displaced from the particular orbitals of the atom. The fitting coefficient is used for correcting variations coming from other factors like background noise. The mass / atomic percentages are calculated by comparing the number of characteristic X- rays of each energy level detected.

Bands achieved at the various energy levels for flyash are graphically represented in Figure 3.7. Peak achieved at 1.486 indicates the presence of Al atoms and peak at 1.739 indicates Si atoms. The atomic weights of Si and Al are 28.08 and 26.982. Flyash shows the presence of impurities like calcium and iron. Metakaolin is relatively pure with Si and Al atoms and other elements are in negligible quantity only. Table 3.10 gives the EDS analysis results of M1 metakaolin. Bands achieved in EDS analysis for M1 metakaolin are given in Figure 3.8.

Table 3.10 EDS analysis for M1 metakaolin

Element	keV	Mass (%)	Counts	Error(%)	Atom(%)	Cation K
O K	0.525	34.99	16793.6	0.01	48.05	1.3221
Al K (Ref.)	1.486	34.28	21753.1	0.01	27.91	1.0000
Si K*	1.739	30.73	19213.0	0.02	24.04	1.0148
Total	-	100.00	-	-	100.00	-

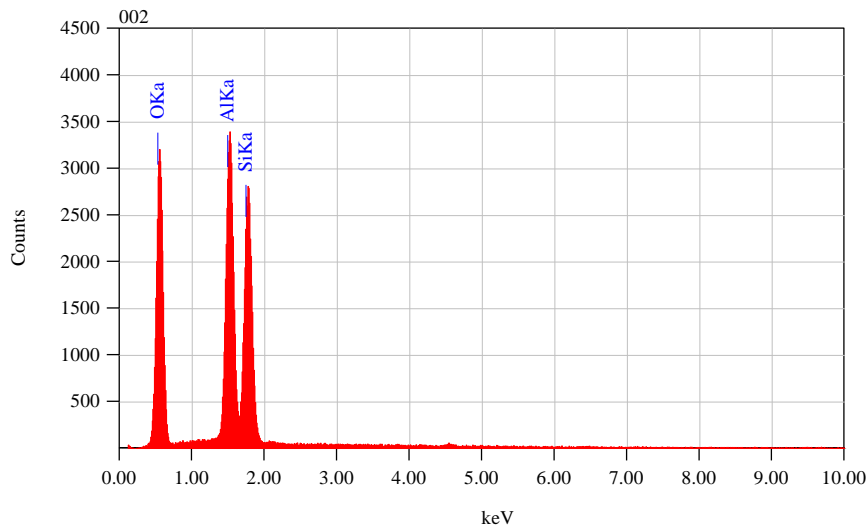


Figure.3.8 EDS analysis for Metakaolin 1 (Si/Al = 0.89)

Table 3.11 EDS analysis of M2 Metakaolin

Element	keV	Mass (%)	Error (%)	Atom (%)	Compound Mass (%)
O K	0.525	48.7	56.62	62.09	56.1392
Al K	1.486	24.23	4.19	18.30	22.5536
Si K	1.739	27.03	5.67	19.61	21.3072

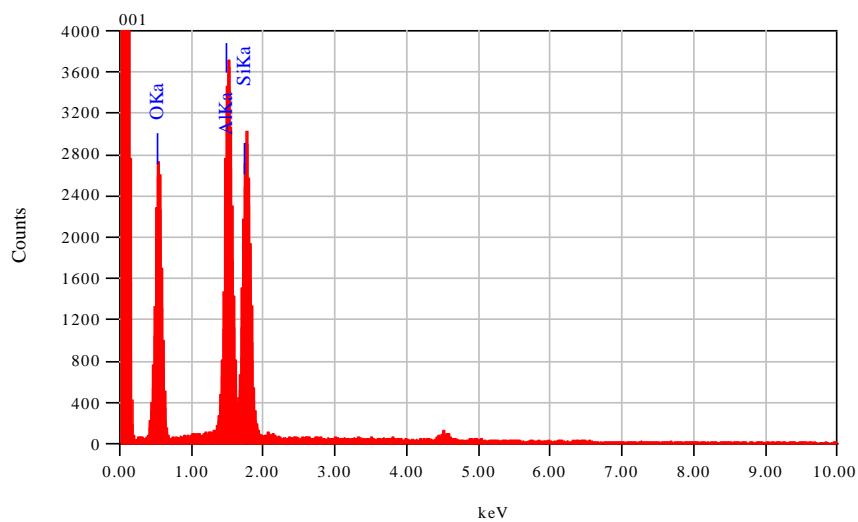


Figure 3.9 EDS analysis for Metakaolin 2 (Si/Al=1.11)

Table 3.11 enlists the mass elemental composition of Si, Al and O in Metakaolin 2. Figure 3.9, shows achievement of a small peak is achieved at 4.508 indicating the presence of Ti in a small amount. Metakaolin M 3 is light red in colour and the EDS analysis results are given in Table 3.12. In Figure 3.10, a small peak is observed at 6.398 indicating the presence of Fe element in small quantity which gives it the particular colour.

Table 3.12 EDS analysis of M3 Metakaolin

Element	keV	Mass(%)	Error(%)	Atom(%)	Compound Mass%
O K	0.525	53.30	3.67	66.29	62.0082
Al K	1.486	21.17	2.52	15.61	18.3560
Si K	1.739	25.54	3.26	18.09	19.6358

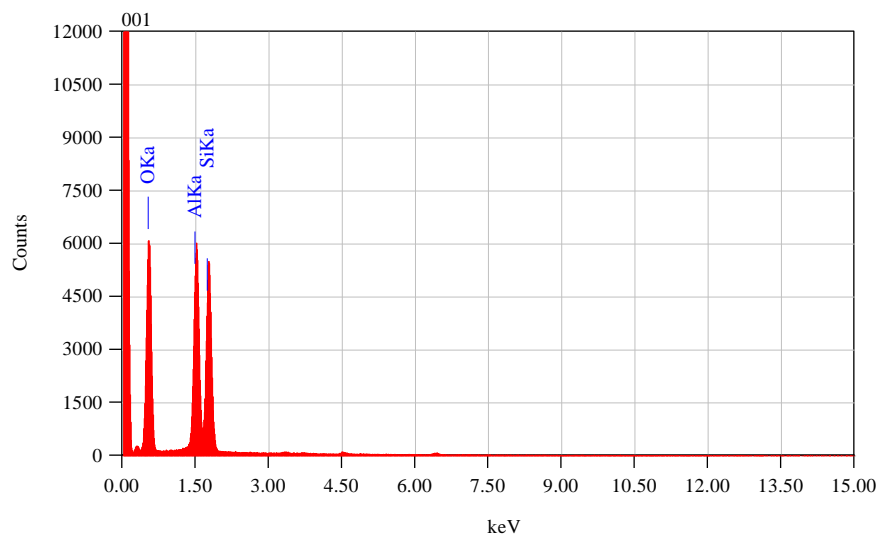


Figure 3.10 EDS analysis for Metakaolin 3 (Si/Al = 1.21)

3.3 Mix proportion

In an attempt to investigate the percentage increase in strength of MK modified concrete, FA is replaced with MK in 25%, 50%, and 75% by mass in geopolymer concrete. Table 3.13 shows the quantity of materials required for

1m³ of GPC. The mix design (Lloyd and Rangan 2010) adopted for 1m³ of geopolymer concrete preparation is as follows.

Assume normal density of concrete	=	2400 kg/m ³
Mass of combined aggregate (77% of mass of aggregate)	=	1848 kg/m ³
Mass of cementitious material and Alkaline Activator(AA)	=	552 kg/m ³
Ratio of AA/cementitious material	=	0.5-0.6
Molarity of NaOH	=	10
Mass of FA/MK	=	552/1.5 =368 kg
Mass of alkaline liquid	=	552-368=184 kg
Ratio of sodium silicate and NaOH	=	2.5
Mass of NaOH	=	52.57 kg
Mass of sodium silicate	=	131.42 kg
Mass of water in sodium silicate at 55.9 %	=	73.46 kg
Solids in NaOH at 285g/ kg of NaOH solution	=	15 kg
Water in NaOH solution	=	37 kg
Total mass of water	=	110.46 kg

Table 3.13 Mix proportion for 1 m³ of concrete

Mix	Flyash (kg)	Metakaolin (kg)	Sand (kg)	Coarse aggregate (kg)	AA solution (kg)
M0	368	-	612	1346	184
M25	276	92	612	1346	184
M50	184	184	612	1346	184
M75	92	276	612	1346	184

3.4 Methodology of the Study

The research methodology followed in this study is presented as a flow chart in Figure 3.11. GPC is seen as a viable alternative to OPC to bring down the CO₂ emission. Practising civil Engineers are sceptical about GPC and more research in this area is needed to convince them. The higher temperature needed for the curing of GPC is a hindrance to the casting of in-situ-concrete. In this study, attempts have been made to synthesize GPC in ambient condition. Slower gain in strength and durability of flyash based GPC is identified as the problem. Previous Literature published provides information on the research findings in this field. Materials are collected to conduct the experimental investigation and preliminary investigations like specific gravity and sieve analysis is done on the materials.

FTIR analysis is done to ensure completion of calcination is complete in M1 metakaolin as it gives rise to lower compressive strength in comparison to flyash in spite of purity, particle size and morphology. EDS and SEM analysis are done for understanding of the microstructure of GP. Trial mixes are cast and tested to arrive at the mix design. The mix is designed and the specimens are cast as required by the tests to be performed on the hardened GPC specimens. Tests have been performed at various ages of curing and results have been

recorded. Metakaolin based GP brick is cast with the strength needed for the practical application and its compatibility and bonding with cement mortar is studied by constructing prisms of various aspect ratio. Compressive strength and Young modulus of MK modified GP brick prism is compared with clay brick prisms. Results are discussed and compared with relevant published results. Conclusions are drawn from the results presented in this experimental investigation.

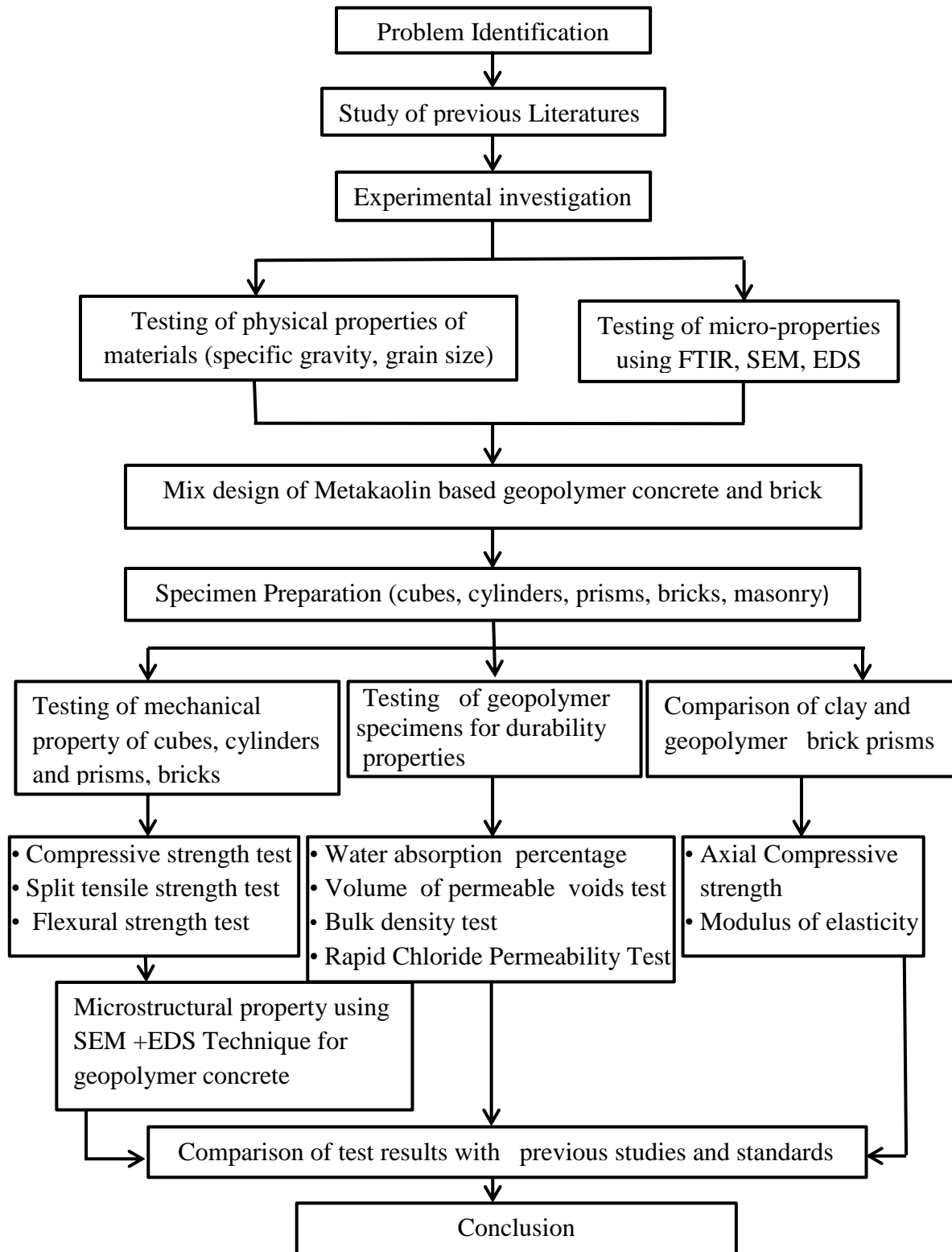


Figure 3.11 Methodology of the Study