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Characterization of Fly Ash from Coal Fired Thermal Power Station

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Abstract - The disposal of fly ash from coal-fired thermal power station is causing economic and environmental problems due to high disposal cost and large area of land required for ash disposal. The generation of huge amount of fly ash has increased the demands for utilization of fly ash as a value-added product used in materials such as cement, bricks, and blocks and in other construction materials. The purpose of this study is to the characterize fly ash sample for potential use. The paper studied the characterization of fly ash samples from thermal power stations were performed by using X-Ray diffraction (XRD), Scanning electron microscopy/Energy-dispersive spectroscopy (SEM/EDS), X-Ray fluorescence spectroscopy (XRF), Dynamic light scattering (DLS) and Fourier transform infrared spectroscopy (FT-IR) techniques. The mineralogical analysis of fly ash was performed by XRD. The morphology and elemental composition of fly ash were characterized by SEM/EDXS. The bulk chemical composition of fly ash was determined by XRF. The particle size distribution of fly ash was analysis by DLS and chemical bonding functional group analysis was studied by FT-IR spectrum.

Keywords: Fly ash, Thermal power station, XRD, SEM/EDXS, XRF, DLS, FTIR.

I. INTRODUCTION

In India, the demand of electricity consumption has increased due to rapid growth of industrialization, urbanization, major infrastructure and economic development. At present about 65% of the electricity consumed in India is generated by thermal power plants accounts two-thirds of the power which includes gas, liquid fuel and coal. Coal is the only natural resource and fossil fuel available in abundance. Consequently, it is widely used as a thermal energy source and also as fuel for thermal power plants producing electricity [1]. In India the electricity generation is mainly dependent upon the coal-based thermal power plants (54.66%) and will continue in the coming several decades due to its large amount reserves. The installed capacity of Thermal Power Stations in India, as on December, 2017for the Year 2016-17 (April2016 to March 2017) was 157377.00 MW from 155 coal based thermal power stations [2]. The coal based thermal power stations generate huge amount of a by-product, fly ash that is a major issue in India. The coal combustion for the generation of electricity results into 30-35% fly ash as a waste product [3]. In India, most of the thermal power plants are using low grade bituminous or sub-bituminous Indian coals with high ash content (30–55%) and low calorific value (3,500–4,000 kcal/kg) [4]. This results in generation of huge quantities of ash every year [5]. Present time generation of fly ash from coal based thermal power plants in Year 2016-17 (April 2016 to March 2017)was169.25 MT[2].Such solid waste required huge land and causes environmental pollution[6] such as adverse impacts on aquatic and terrestrial ecosystems due to leaching of toxic substances from the ash into ground water and soil[7].However, the current utilization of fly ash is only about 56% i.e. 107.10 MT mainly in the areas of cement as well as concrete manufacturing, bricks making, road construction and building products, and to some extent in earth fills [2], [8]. The rest of fly ash generated by the coal based power station is disposed of by using wet or dry systems. In the dry ash disposal system ash is stored in form of ash mounds and by the action of rain the present of heavy metals get leached and reach to the water of ponds, rivers etc. In the wet disposal system ash is mixed with water and the ash slurry is transported to the disposal area- ash ponds as wet slurry. In ash pond the fly ash come in contact with water continuously and leaching out of heavy metal in ash pond that contaminates to soil, water environment due to heavy metal contamination [9] and the deterioration of several ecosystem. There are several types of heavy metals which are released from fly ash leachates such as cadmium, lead, zinc, chromium, copper, nickel, and arsenic etc. [10].It is now widely realized that fly ash should be accounted as a useful mineral resource and the development of technologies for high value-added utilization of fly ash is important [11]. The understanding of the characteristics of ash particles and the transformation of coal minerals during combustion are essential to the development of value-added ash utilization technologies. Fly ash can be treated as a by-product rather than waste.

Fly ash is defined in Cement and Concrete Terminology (ACI Committee 116) as the 'finely divided residue resulting from the combustion of ground or powdered coal, which is transported from the fire box through the boiler by flue gases'. It is composed of very fine particles that are carried by flue gases away through chimney and collected by the electrostatic precipitator (ESP) hoppers. Fly ash is fine glass powder, the particles of which are generally spherical in shape and micron sized earth element range in size from 0.5 to 100μm. Fly ash is classified into two types according to the type of coal used. Anthracite and bituminous coal produces fly ash classified as class F. Class C fly ash is produced by burning lignite or sub-bituminous coal [12], [13]. Fly ash consists of mainly ferro-aluminosilicate materials. When fly ash is mixed with lime and water it forms a cementitious compound that is the properties of similar to Portland cement. Being this similarity, fly ash can be used to replace a portion of cement in the concrete and also used as a valuable raw material for fly ash bricks, blocks, cement and other construction materials.

In the present study a chemical, elemental composition, mineralogical and morphological structural characterization of fly ash generated from Gandhinagar Thermal Power Station. The aim of this study was to investigate the possibility of use of fly ash in materials such as cement, bricks, blocks and other materials. Analysis such as X-Ray Diffraction (XRD), Scanning electron microscopy/Energy-dispersive spectroscopy (SEM/EDS), X-Ray Fluorescence (XRF), Dynamic light scattering (DLS) and Fourier Transform Infrared Spectroscopy (FT-IR) were performed to characterize fly ash. Depending on the results of the analysis, mineralogy, morphology, elemental and chemical composition, particle size distribution and chemical bonding of fly ash was investigated.

II. MATERIALS AND METHODS

2.1. Samples

The fly ash sample have been used in the present study was collected from the hopper below the electrostatic precipitator (ESP) from thermal power station. The samples were provided by the Gandhinagar Thermal Power Station, Gandhinagar, Gujarat.

2.2. Characterization of fly ash sample

Firstly the fly ash samples were subjected to sieving and fly ash samples were dried at 105°C for 24 hours. Fly ash was characterized by using different analytical equipments such as XRD, SEM/EDS, XRF, DLS and FTIR.

2.3. Equipments

In the present study the sample has been characterized by the following equipments. The samples were prepared in different manners for the characterization of fly ash.

2.3.1. X-ray diffraction (XRD) analysis

Crystalline structure and mineralogy of the fly ash sample were determined by conducting High Resolution X-Ray diffractometer. HR-XRD data usually measures scattered X-ray intensity as a function of omega and/or 2theta.Diffraction patterns are produced by the coherent scattering of light by atoms in crystalline materials. The data files presented by X'Pert Graphics and Identify data collection software were used to identify the minerals phases present in the samples.

2.3.2. Scanning electron microscope and Energy dispersive spectroscopy (SEM-EDS) analysis

A High resolution scanning electron microscope (HRSEM) with energy dispersive spectroscopy (EDS) was used to study the morphology, texture and elemental composition of the fly ash samples. Scanning Electron Micro analyzer was used to take the micrograph of the sample. Sample was mounted on aluminum stubs using conductive glue and was then coated with a thin layer of carbon. A further use of the SEM was the analysis of discrete samples and the carrying out of quantitative analysis on separate grain-sized fractions. The energy dispersive spectroscopy (EDS) was used to determine the elemental composition of manually chosen areas in the fly ash particles.

2.3.3. X-ray fluorescence (XRF) analysis

Chemical compositions and bulk elemental analysis of fly ash were determined by XRF. A Horiba XGT-2700 X-ray analytical microscope equipped with an X-ray tube with Rh target detector high purity silicon detector (XEROPHY) was used. A vacuum was used as the medium of analyses to avoid interaction of X-rays with air particles. The samples were ground to <75µm in a tungsten carbide milling vessel. A mixture of 1g sample and 6g $Li_2B_4O_7$ was then fused into a glass slide. Major element analyses were executed on the fused bead.

2.3.4. Dynamic Light Scattering (DLS) analysis

The particle size distribution pattern of fly ash particles was determined with the help of a dynamic light scattering technique (Model: NPA152-31A-000-000-90M, Make: Metrohm) based on intensity fluctuation. The measurements were made in liquid mode, with a measurement range of 1 to 10000 nm.

2.3.5. Fourier transform infra-red (FT-IR) analysis

The Perkin Elmer FTIR spectrometer was used in the present work for recording the FTIR spectra of the samples at room temperature. FTIR was used in identification of chemical bonds and functional groups of samples. The KBr pellet technique (1:20) was followed for the mineral analysis. To provide a good characterization of a mineral by infrared spectroscopy, the spectrum recorded in the range of 4000-400 cm^{-1}at ambient temperature and the resolution used was $4cm^{-1}$.

III. RESULTS AND DISCUSSION

High disposal cost and large area of land required for disposal of ash demands utilization of fly ash to the maximum extent. In India, fly ash generation and utilization was during the year 2016-17 was 169.25 and 107.10 million-tons respectively. The percentage of fly ash utilization was 56.04. The maximum utilization of fly ash to the extent of 23.98% of total fly ash utilized was in cement sector followed by 8.81 % in making bricks and tiles, 6.25 % in reclamation of low lying area, 6.96 % in mine filling, 7.02 % in ash dyke raising, 3.66 % in roads and flyovers, 1.14% in agriculture, 0.45% in concrete and 4.72 % in others, etc. [14]. The utilization of fly ash as an engineering material primarily stems from its pozzolanic nature, spherical shape, and relative uniformity. The samples of fly ash of thermal power station were analyzed by XRD, SEM-EDS, XRF, DLS, FTIR and the mineral phase, morphology, compositions of several elements, particle size, functional group present in the samples were determined.

3.1. Mineralogical composition of fly ash by X-ray diffraction (XRD)

XRD analysis was conducted of the fly ash sample and the results are shown in Figure 1 and Table 1. Result obtained by XRD showed that illite-montmorillonite is the predominant crystal constituent in the fly ash sample. The mineralogical composition identified by XRD in the fly ash was abundant illite-montmorillonite, mullite and quartz. The XRD peak intensities (count values) of the fly ash samples very low, suggesting that non-crystalline amorphous (glass) phase are main constituents of the fly ash. The crystalline constituents in the fly ash include the minerals illite-montmorillonite, mullite and quartz.

Table1. XRD Result of fly ash

Phase Name	Chemical Formula
Illite-montmorillonite	$K\ Al_4\ (Si, Al)_8\ O_{10}$
Mullite	$3Al_2O_3SiO_2$
Quartz	SiO_2

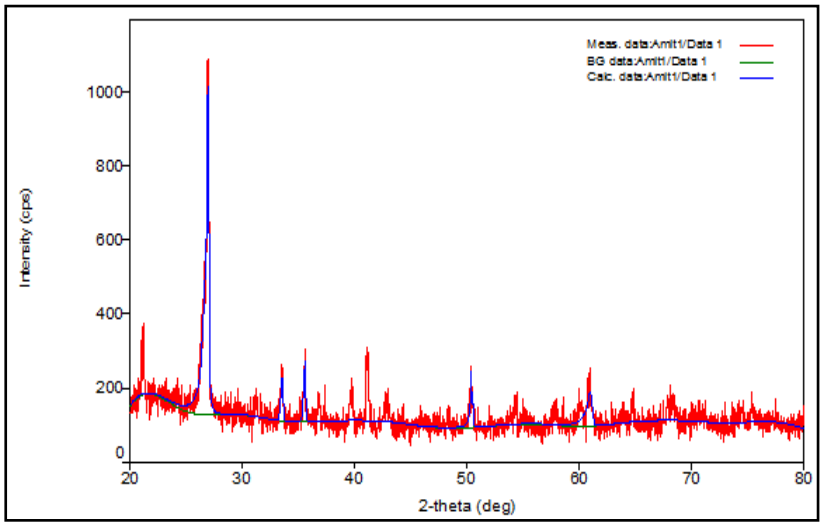

Figure1. XRD patterns of fly ash

3.2. Morphology of fly ash by SEM-EDS

SEM is one of the best and most widely used techniques for the characterization of fly ash. A high resolution scanning electron microscope (HR-SEM) with energy dispersive X-Ray spectroscopy (EDS) was used in this experiment to determine the morphology, texture and elemental composition of fly ash sample. The analysis results obtained from HR-SEM with EDS measurements are shown in Figure 2 and 3. Figure2 shows the surface morphology of the particles of fly ash is irregular in their shape and majority of particles are solid. It can be seen that fly ash are generally composed of mainly small, spherical alumino silicate particles along with larger irregular carbon particles. The rounded particles with a large distribution in size are predominantly glassy. The angular particles are mainly comprised of crystalline solids such as quartz, mullite, magnetite and hematite. The spherical particle which is corresponds to magnetic fraction of fly ash sample. The non-magnetic elements have a general tendency to be spheroid. With increase in particle size this spheroid nature of the magnetic properties increases. Some particles are spherical in shape or hollow. Occasionally, cenosphere particles may be observed under SEM. The elemental composition of fly ash sample was determined by EDS shown in Figure 3 and Table 2. EDS results showed that Fly ash sample were predominantly contains O, C, Al, and Si with traces elements were K, Fe, Mg, Na and Ti in the sample.

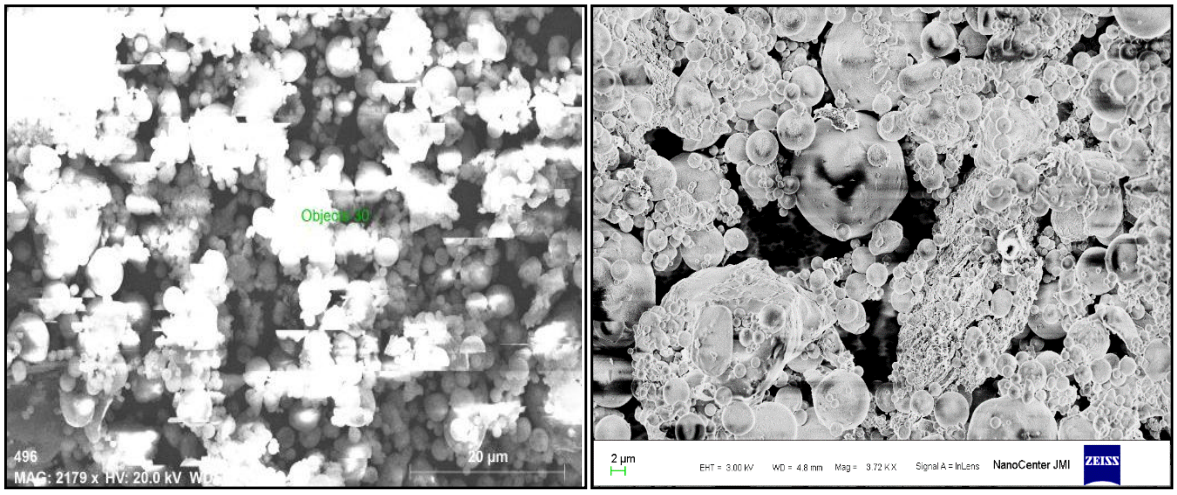

Figure 2. SEM image of fly ash

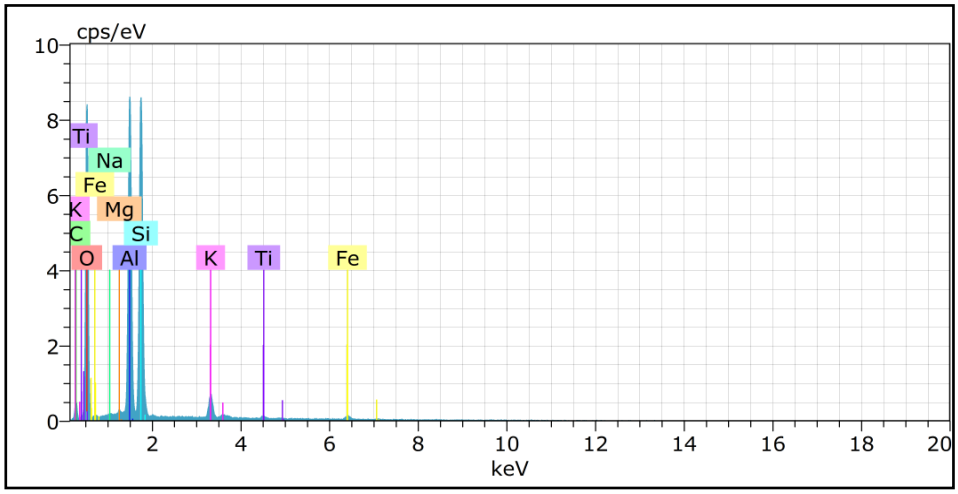

Figure 3. EDS spectra of fly ash

Table 2. Elemental composition of fly ash

Element	Weight %	Atomic %
O	59.65	67.43
C	7.81	11.76
Al	15.00	10.06
Si	14.50	9.34
K	1.66	0.77
Fe	0.75	0.24
Mg	0.22	0.16
Na	0.21	0.16
Ti	0.21	0.08

3.3. Chemical composition of fly analysis by XRF

X-ray fluorescence (XRF) was used to determine the chemical compositions of the major, minor and trace elements of the fly ash. The analyzed results are given in Table 3and shown spectrum in Figure 4. Figure 4 shows the elements which are present in fly ash. It can be seen in Table 3 that the major compositions of fly ash samples are silica, alumina and iron oxide. These oxides account for 90%. The most abundant oxides in the fly ashes are those of Si, Al and Fe followed by Na, Ti, K, Ca, Mn, Cr, S, V, Cu, Zn, Sr, Co, As, Ni and Br. Fly ash has a CaO content <1%. The composition of fly ash indicates of class F type fly ash. We observed that the major elements in all fly ash samples are Si, Al and Fe and the other Ti, K, Ca, Mn, Cr, S, V, Cu, Zn, Sr, Co, As, Ni and Br elements occur as minor constituents. The elemental analysis of these samples will be informative to use the fly ash for various applications such as cement manufacturing, ceramic production and as a secondary source in recovery of valuable elements.The present of SiO_2 and Al_2O_3in fly ash shows a good correction with long-term pozzolanicactivity[15] although SiO_2 and Al_2O_3in an amorphous form only contribute tothe pozzolanic activity.

Table3. Chemical composition of fly ash samples

Compounds	Mass [%]
SiO_2	60.13
Al_2O_3	25.983
Fe_2O_3	5.44
Na_2O	3.93
TiO_2	2.329
K_2O	0.939
CaO	0.922
MnO_2	0.055
Cr_2o_3	0.047
SO_3	0.036
V_2O_5	0.036
CuO	0.035
ZnO	0.025
SrO	0.024
CoO	0.023
As_2O_5	0.022
NiO	0.013
Br_2O	0.009

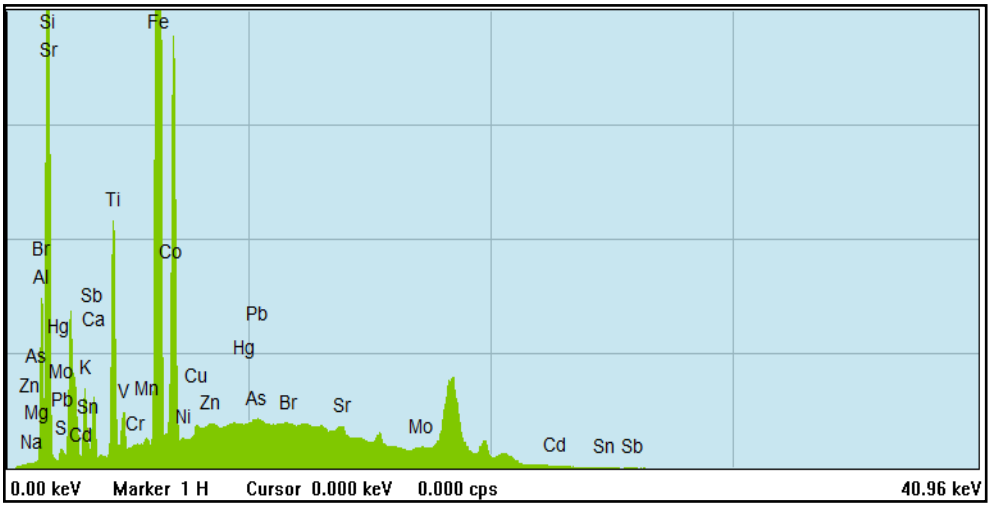

Figure 4. XRF spectra of fly ash

3.4. Particle size distribution of fly ash by DLS

DLS technique was used for measuring the particle size distribution of fly ash. The wide range of particle size distribution in fly ash is shown in Figure 5. The results showed that fly ash contains more fine particles sized small than 4580 nm. The particle size distribution of fly ash use to be between 3150 nm and 4580 nm. Fly ash has approximately 50% of particle sized lower than 3670 nm. Particle size distribution is the physical characteristics of the fly ash which is mostly affect their reactivity and their use as pozzolans. Pozzolanic reaction property increases with the increase of fineness properties [16] (Demir et al., 2002). The fineness of fly ash is affected by pulverisation of coal, thermal process and type of elctroprecipitator installed in power station.

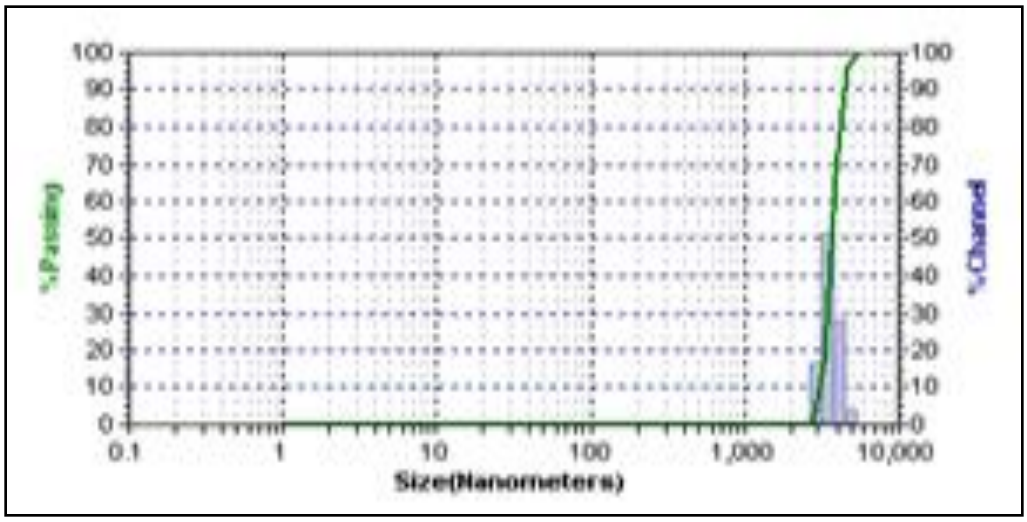

Figure 5. Particle size distribution of fly ash

3.5. FTIR spectroscopic analysis of fly ash

The FTIR spectrometer (Perkin Elmer) was used in the present study for recording the FTIR spectra of the fly ash samples at room temperature to determine their functional group, bonds and reactivity. The KBr pellet technique (1:20) was followed for the mineral analysis. To provide a good characterization of a mineral by infrared spectroscopy, the spectrum recorded in the range of 4000-450 cm. The FTIR spectrum of the fly ash is shown in Figure 6. The important infrared (IR) bands of samples with their possible assignments are given in Table 4. By comparing the observed frequencies with available literature, the minerals such as montmorillonite, quartz, hematite and feldspar have identified. Figure 6. Show a broad band between 450 and 3500 cm^{-1}. Five characteristic band centered at around 3484, 1094, 795, 558 and 463 cm^{-1} has been identified. The strong and broad band at 1094 cm^{-1} is due to (Si-O-Si) asymmetric stretching vibration [17]. Fly ash sample centered at this band has the highest SiO_2 content. The bands at 795 cm^{-1} attributed to (Si-O) due to symmetric [17], [18]. The other two bands at 558 and 463 cm^{-1} are attributed to (Si-O-Al) and (Si-O-Si) vibration respectively [19], [20]. The most prominent peaks in the spectra area of the fly ash, consisting of silica aluminium glass, and originate from Si-O-Si and Si-O-Al stretch vibrations. The peaks are quite broad and no evidence of other crystalline phase could be observed in the spectra as montmorillonite, quartz, hematite and feldspar have peaks in the different regions as the glass.

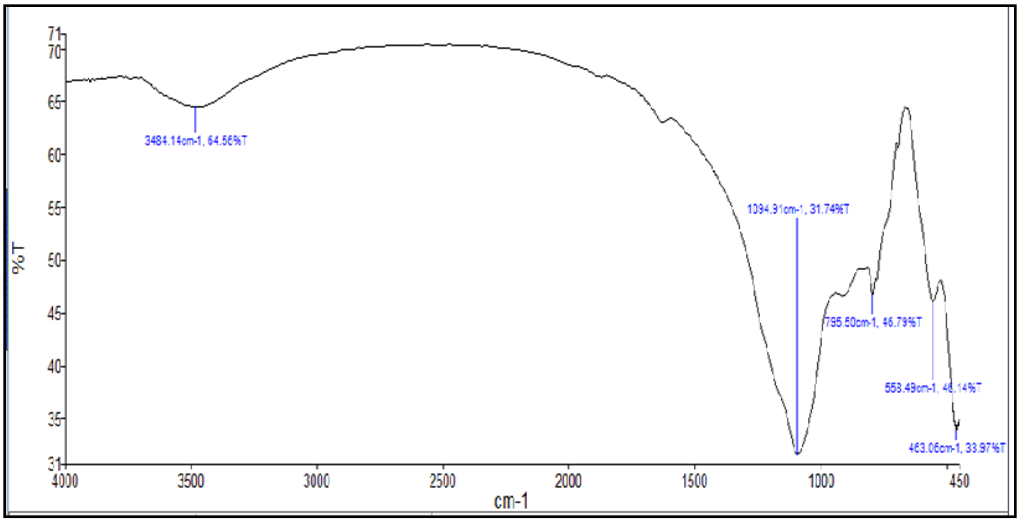

Figure 6. FT-IR spectra of fly ash

Table 4. Band assignments for different minerals of fly ash

Frequency (cm^{-1})	Mineral Name/component	Tentative Assignment	References
3484	Montmorillonite	OH group of adsorbed water dust-stretching	[21]
1094	Quartz	Si-O-Si asymmetric stretching vibration	[17]
795	Quartz	Si-O symmetric	[17], [18]
558	Hematite	Si-O–Al (or) Fe2O3	[19]
463	Feldspar	Amorphous silica Si-O-Si band	[20]

IV. CONCLUSION

The characterization of fly ash samples produced in Gandhinagar Thermal Power Plant has been examined. In the present study, the result of XRD analysis showed that mineral composition illite–montmorillonite and mullite are the major crystalline phases in fly ash. Morphology of fly ash particle is irregular, small rounded, spherical particles with both amorphous structures and crystalline solid showed by SEM. The results of EDXS showed that fly ash samples mainly predominant the elements of oxygen, aluminium, silicon and low content of iron, calcium, and potassium. The results of XRF revealed that the predominant compositions of fly ash samples are silica, alumina and iron oxide. FTIR spectra for samples showed peaks associated with montmorillonite, quartz, hematite and feldspar. The fly ash samples contain significant amount of fine particles with the diameter smaller than 4580nm. Result obtained in this study showed that fly ash is of the ASTM type F, which has excellent pozzolanic properties. The materials will be beneficiated to allow a higher quality value additive material. Possible utilization for these fly ashes in India context is suggested. These uses would have economic benefits and also eliminate the disposal of fly ash with its associated environmental hazards and drawbacks. By this study, through the characterization of this waste-fly ash will be turned to be a resource material in construction product either as direct substituent of cement or as admixture in concrete, bricks and other materials.

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