

Ball Milling of Class-F Indian Fly Ash Obtained from a Thermal Power Station

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Abstract—Fly ash (FA) is a waste material produced by combustion of coal. Large quantities of FA have been generated worldwide from thermal power stations. Many routes have been tried for the safe disposal of FA. In an effort to add value to FA, a class-F FA that has been generated by a thermal power station was subjected to high energy ball milling. Ball milling was carried out for a total duration of 60 hrs and samples were taken out at regular intervals for characterizing various properties of the ball milled FA. Crystallite size and particle size of the ball milled FA were determined by X-ray diffraction and dynamic laser scattering, respectively. The shape and texture were studied using SEM and TEM. IR Spectroscopy revealed that the smooth and inert surface of the FA was converted to a rough and more reactive one by ball milling. It was found that after 60 hrs of milling, crystallite size of quartz phase present in the FA was reduced from 37.58 nm to 9.25 nm and the average particle size got reduced from 94.35 μm to 0.70 μm .

Keywords—Fly Ash; High Energy Ball Milling; Nanomaterial; Waste; Electron Microscopy

I. INTRODUCTION

There is currently an extraordinary amount of interest in *nanomaterials* and *nanotechnology*. The term *nano* is derived from the Greek word for *dwarf*. It is used as a prefix for any unit such as a second or a meter, and it means a billionth of that unit [1, 2]. Nanomaterials and nanotechnology have been developed as a consequence of remarkable advances in the material science community.

A nanomaterial is defined as one that has at least one dimension in nanometer range. It has appeal of miniaturization; also it imparts enhanced electronic, magnetic, optical and chemical properties to a level that cannot be achieved by conventional materials [3].

Essentially there are two different approaches for creating very small machines or devices. First there is the increasingly precise ‘top-down’ approach of taking a block of material and whittling it away to the object that is wanted. The second approach is called the ‘bottom-up’ approach, where individual atoms and molecules are placed or are self-assembled precisely where they are needed. Here molecular or atomic building blocks are designed fitting together to produce bigger objects [4]. Nanomaterials are not new. However certain preparations of oxides, metals, ceramics and other substances of nanomaterials are relatively understood recently.

There are various methods to produce nanomaterials, like plasma arcing, chemical vapour deposition, electro-deposition, sol-gel synthesis, and ball milling. In the first two methods, molecules and atoms are separated by vaporization and then allowed to be deposited in a carefully controlled and orderly

manner to form nanoparticles. The third method, electro-deposition, involves a similar process, since individual species are deposited from solution. The fourth process, sol-gel synthesis, involves some prior ordering before deposition. In ball milling, known macro-crystalline structures are broken down into nano-crystalline structures, but the original integrity of the material is retained. However, the nanoparticles can reform into new a material, which involves breaking the original crystalline bonds. Among these methods high energy milling has the advantages of being simple, relatively inexpensive, and applicable to any class of materials which can be easily scaled up to large quantities [5].

FA is a waste product generated from coal fired thermal power stations. Large number of coal fired thermal power plants all over the world dispose a huge quantity of FA causing serious environmental problems [6]. During the process of (coal) burning, according to an estimate, about 112 million tons of FA have been presently generated per annum in India alone, whose level is to be further raised with the installation of more new thermal power plants by 2020 [7]. FA causes great health hazards and environmental pollution, and the situation has worsened to the extent that even dumping of ash is becoming a problem because of the shortage of space required to accommodate the large volume of its generation. As the raw materials are being consumed at a faster rate than they are being replaced, it becomes necessary to think about efficient use of natural resources and reuse and recycling of industrial wastes. The accumulation and disposal of industrial wastes like FA are of national and international concerns [8, 9].

In this work, an attempt has been made to modify fly ash by transforming the micro sized FA into nanostructured FA using high energy ball milling. Thus nano FA can be used to reinforce filler in making polymer composites. The ball milled FA was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared (FTIR) spectroscopy and Dynamic laser scattering.

II. EXPERIMENTAL DETAILS

A. Sample Preparation

FA was obtained from Thermal power station, Tuticorin, Tamilnadu, India. Loss on ignition, which was measured by burning the sample in a muffle furnace at 800 °C for 3 hrs, was 2.78 %. Fresh FA was washed in distilled water and the carbon that creamed up during washing was removed. It was then dried at 100 °C for 24 hrs to remove water. Dried FA was

sieved using British Standard Sieve (BSS). FA fractions that passed through mesh no. 170, but got retained on mesh no. 240 were collected and magnetic separation was carried out manually to remove the magnetic impurities. Then this FA was taken for ball milling.

B. High Energy Ball Milling

Reduction in particle size of the FA from μm to nm level was achieved by using a high-energy planetary ball mill (model PM 100; Retsch, Germany). The following milling conditions were maintained: the ball mill was loaded with balls at 10:1 ratio to FA; milling chamber and balls were made of tungsten carbide; the ball diameter was 10 mm. Toluene was used as the medium and ball milling was carried out in the presence of sodium lauryl sulphate as the surfactant to avoid agglomeration of the ceramic particles in FA, at a ratio of 100:1 of FA to surfactant; rotation speed of the planetary carrier was 300 rev.min^{-1} . Samples of the milled powder were taken out at an interval of 10 hrs and dried in a hot air oven at 80°C for 6 hrs.

C. X-Ray Diffraction

X-ray diffraction measurements were carried out to find the crystallite size of the quartz phases of fresh and ball milled fly ashes, with the help of a Goniometer (model: JEOL DX-GE-2P, Japan) using CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$) at an accelerating voltage of 30 kV and a current of 20 mA. The samples were scanned at a speed of 2 deg.min^{-1} in the 2θ range from 10 to 90° .

D. Infrared Spectroscopy

A Fourier Transform Infrared Spectrophotometer (model: Nicolet Avatar 330 FT-IR, USA) was employed for examining the functional groups of the fresh as well as ball milled FA samples in ATR mode in the wave number region from 400 to 4000 cm^{-1} .

E. Morphology Studies

A Scanning Electron Microscope (SEM) (model-JEOL-JSM-6380LA, USA) with energy dispersive X-ray spectroscopy (EDXS) (Link ISIS-300 Micro-analytical System, Oxford Instruments, UK) was used to evaluate the texture, morphology and elemental composition of fresh and ball milled fly ashes. The FA was sputtered with gold in a sputtering unit (model: JEOL JFC 1600, USA), auto fine coater, to make their surfaces conductive. The images were taken at suitable accelerating voltages for the best possible resolution using secondary electron imaging. A transmission electron microscope (Philips CM 200) was used for the analysis of particle surface as well as surface texture.

F. Particle Size Analysis

Particle size analysis of fresh and ball milled fly ashes was determined by dynamic laser scattering (Mastersizer- Malvern Instruments, UK). During the particle size measurement, fly ash particles were passed through a focused laser beam. These particles scattered light at an angle that is inversely proportional to their size. The angular intensity of the scattered light was then measured by a series of photosensitive detectors. The number and positioning of these detectors in the Mastersizer has been optimized to achieve

maximum resolution across a broad range of sizes.

III. RESULTS AND DISCUSSION

A. Morphological Studies

Surface texture and shape of the fresh as well as ball milled fly ashes were studied by Secondary Electron Imaging (SEI) mode of Scanning Electron Microscope (SEM). Fig.1 shows the SEM micrographs of fresh and ball milled fly ashes. Majority of the particles in the fresh FA are spherical in shape and have smooth surfaces (Fig. 1A). The morphology of FA particles is controlled by combustion temperature and cooling rate. The furnace operating temperature of pulverised coal fired boiler is usually higher than 1400°C [10]. At these high temperatures, the inorganic materials in coal become fluid-like and solidify, leading to different morphologies of generated FA. Due to rapid cooling inter-particle fusing occurs and FA particles agglomerate, which results in irregular shape [7, 11].

Fig.1 (B) is the photomicrograph of the FA after 20 hrs of ball milling. The spherical structure of fresh FA has been destroyed and the average particle size was reduced [12]. Fig. 1 (C) and 1 (D) shows the images of 40 hrs and 50 hrs ball milled samples of whom the structural breaks is more.

Fig.2 (A) is SAED (selected area electron diffraction) pattern of FA, which is in polycrystalline state even after being milled for 60 hrs. The individual crystals are present at different orientations; thus, if the diffraction aperture used is larger than the crystal size, then the diffraction pattern is the sum of each individual crystal. Because only certain planes can diffract, the spots are now randomly distributed but then fall on rings of constant radius. The smaller the crystal size is, the larger the number of crystals will be included in the diffraction rings [13].

Fig.2 B-D show the high magnification TEM micrographs of single particles from FA sample that was ball milled for 60 hrs. These images show that the size of the single FA particle is in the nanometer range after 60 hrs of ball milling. Thus, nano-structured materials are proven to be present in the ball milled FA. Also the surface of the FA has changed from being glassy and smooth to being irregular and rough.

Chemical composition of FA was determined by Energy Dispersed X-ray analysis (EDX) and elements presented in it are shown in Fig. 3. FA has been classified into two categories, Class F and Class C. The FA that contains more than 70% of oxides of silicon, aluminium and iron of the total composition with higher Fe_2O_3 content than CaO is termed as Class F type [14, 15]. According to the calculations carried out based on EDX analysis the overall composition of FA obtained for this study consists of major proportion of SiO_2 , Al_2O_3 and Fe_2O_3 , which amounts up to 93.58%. Table I shows the values of elemental composition and the relative % of the oxides obtained from an average of readings recorded at 10 different locations on the fresh FA sample. It is observed that percentage of calcium oxide, which is 0.51%, is less than that of iron which is 4.7%, which reveals that the FA belongs to Class F [16, 17].

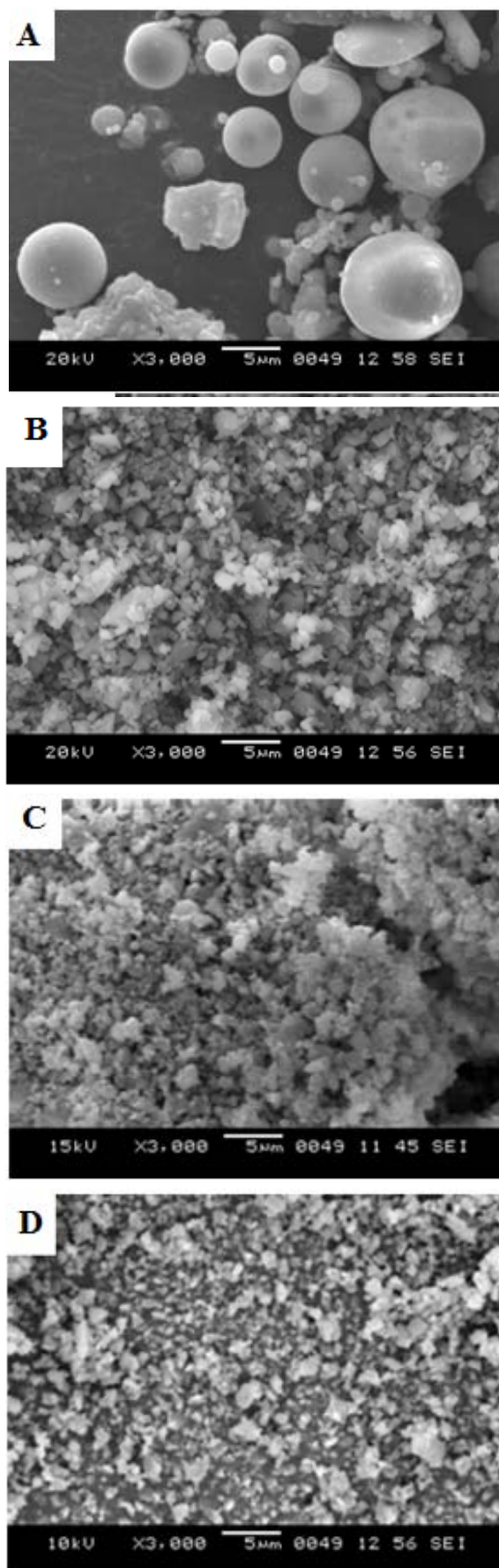


Fig. 1 Scanning electron micrographs of fresh and modified FA. (A) SEM of fresh FA, (B) SEM of ball milled FA for 20 hrs, (C) SEM of ball milled FA for 40 hrs, (D) SEM of ball milled FA for 60 hrs.

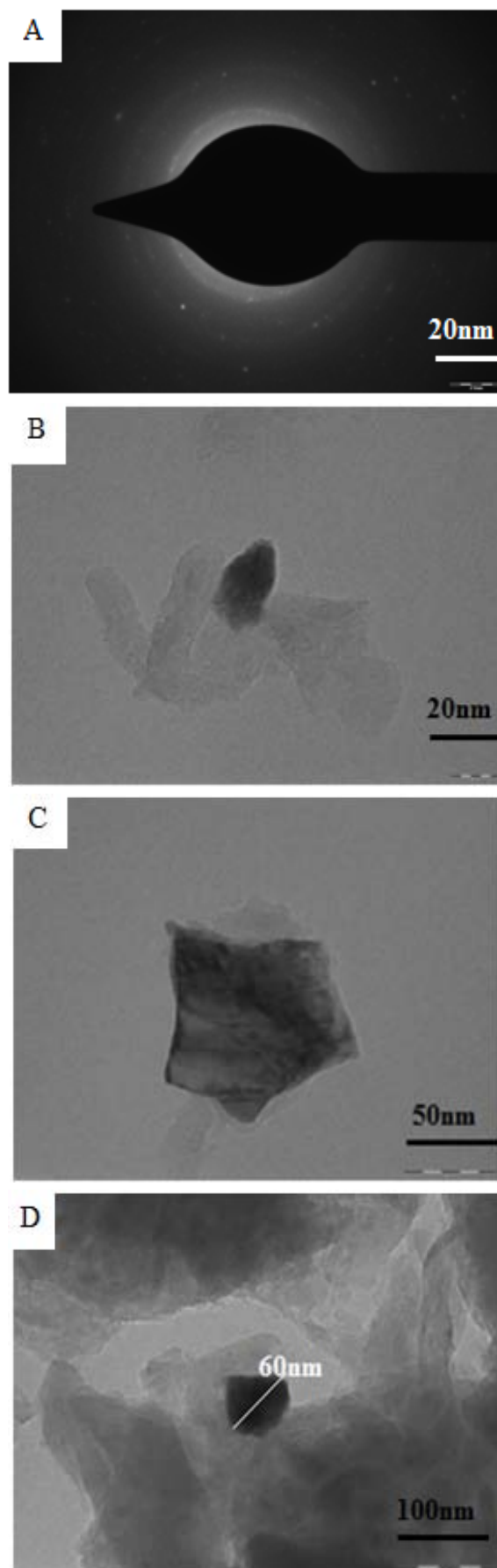


Fig. 2 (A) SAED Pattern and (B–D) TEM micrographs of FA milled for 60 hrs.

TABLE I
COMPOSITION OF FRESH FLY ASH

% Elemental Composition		% Oxide Composition	
component	Content (%)	Component	Content (%)
Silicon	31.01 ± 0.2	SiO ₂	56.06 ± 0.2
Aluminium	16.53 ± 0.2	Al ₂ O ₃	32.82 ± 0.2
Iron	2.2 ± 0.2	Fe ₂ O ₃	4.7 ± 0.2
Titanium	1.04 ± 0.2	TiO ₂	2.3 ± 0.2
Potassium	0.94 ± 0.2	K ₂ O	2.06 ± 0.2
Sodium	0.38 ± 0.2	Na ₂ O	0.82 ± 0.2
Calcium	0.23 ± 0.2	CaO	0.51 ± 0.2
Magnesium	0.32 ± 0.2	MgO	0.71 ± 0.2
Oxygen	47.34 ± 0.2	Total	99.98 ± 0.2

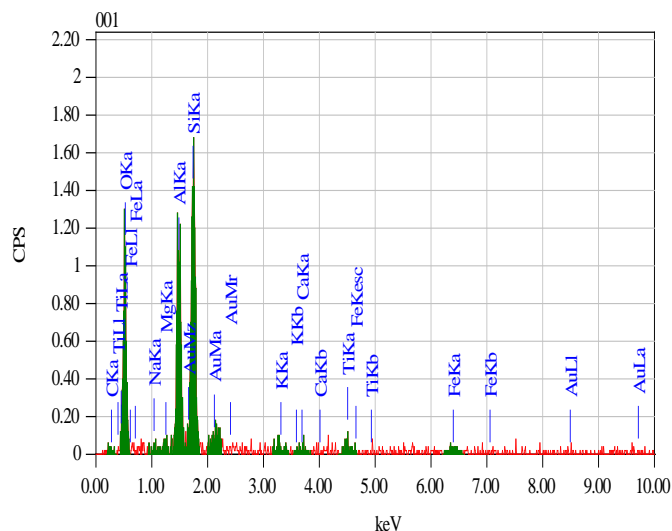


Fig. 3 EDX results of fresh fly ash.

B. X-Ray Diffraction Results

X-Ray diffractograms of fresh as well as ball milled FA are given in Fig. 4. It can be clearly observed that peak intensity of quartz phase is reduced and the peaks broaden as the duration of milling was increased as shown in Fig. 5. The average crystallite size was determined by the full width at half maximum (FWHM) of the X-ray diffraction peak using Scherrer's equation.

$$t = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where t is the particle diameter, λ is the X-Ray wavelength, β is the FWHM of the diffraction peak, θ is the diffraction angle and k is the Scherrer's constant of the order of unity for usual crystals [18]. Ball milled FA exhibits lower degree of crystallinity, but it shows a number of crystalline peaks in the diffractogram. Mullite (Alumina silicate) shows peaks at 25.82°, 27.20° at 2θ values (d spacing of 3.45 and 3.4 Å). The quartz exhibits peaks at 20.73°, 26.52°, 26.66°, 40.66°, 49.96° at 2θ values (d spacing of 4.28, 3.36, 3.34, 2.21, 1.82 Å) and iron oxide and calcium oxide at 33.08° and 60.42° at 2θ values (d spacing of 2.70 and 1.53).

An amorphous hump is observed in the diffraction pattern between 2θ values of approximately 14° to 35°, which could be due to the presence of amorphous glassy materials. Fig. 6

displays the reduction in crystallite size of the quartz phase from 37.58 nm to 9.25 nm with increase in milling time. A steady decrease in the crystallite size is observed as shown in Table II, thus increasing the amorphous domains in it [15, 19]. This change is beneficial to applications such as particulate nano-filler in polymeric matrices. The enhanced amorphous content is very encouraging as it may lead to better compatibility with various polymeric matrices.

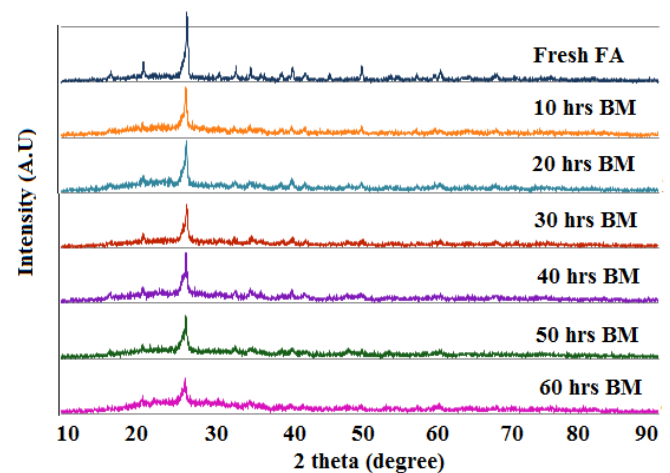


Fig. 4 X-Ray diffraction patterns of fresh and ball milled FA at different times.

TABLE II
CRYSTALLITE SIZE OF QUARTZ PHASE IN FRESH AND BALL MILLED FA

Samples	Crystallite size (nm)
Fresh FA	37.58
10 hrs BM	25.32
20 hrs BM	17.15
30 hrs BM	15.94
40 hrs BM	11.52
50 hrs BM	11.05
60 hrs BM	9.25

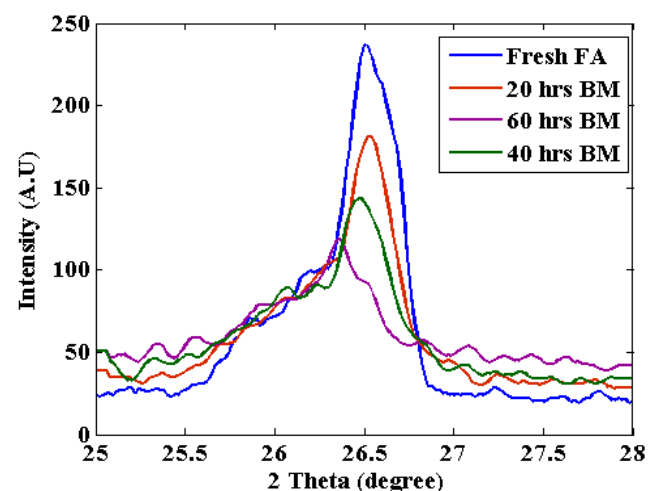


Fig. 5 Variation in the quartz peak ($2\theta = 26.58^\circ$) height and width with duration of milling.

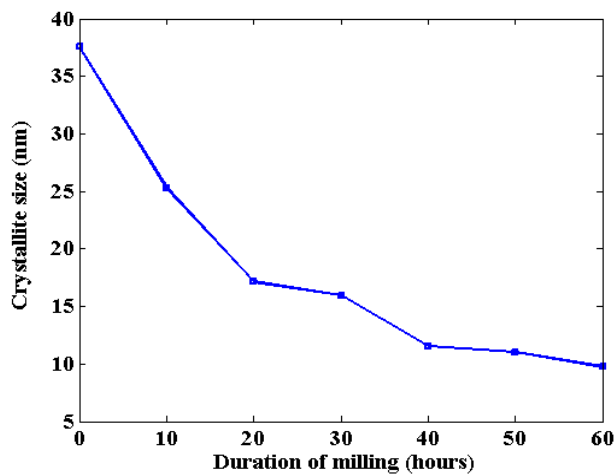


Fig. 6 Variation of crystallite size of quartz phase with milling duration

C. Infrared Spectroscopy

Fig. 7 shows the FTIR spectra of fresh as well as 60 hrs ball milled FA. The important infrared (IR) bands of FA with their possible assignments are shown in Table III. The peak at 1092 cm^{-1} has broadened in milled FA as compared to fresh FA, which is Si-O-Si stretching [20]. The peak at 3422 cm^{-1} which was insignificant in the fresh FA, has become conspicuous in case of ball milled FA, this is because of its interaction with the surfactant. This has been attributed to the presence of silanol (Si-OH) functional groups in the FA [19, 21]. That the peak intensity at this wave number is found to increase with increasing milling time is an evidence for the breaking down of the quartz structure and formation of Si-OH groups. The peak intensity of Si-O-Fe stretching at 444 cm^{-1} is found to decrease due to the magnetic separation [22, 23].

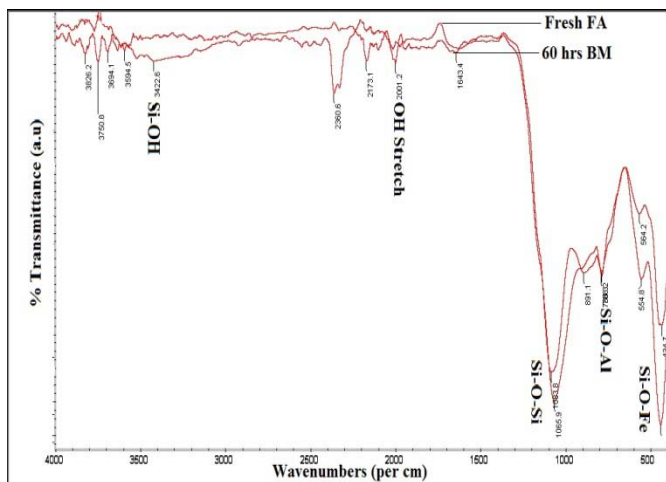


Fig. 7 FTIR spectra of fresh FA and 60 hrs ball milled FA.

TABLE III
IMPORTANT IR BANDS OF FA WITH THEIR POSSIBLE ASSIGNMENTS

Observed band (cm^{-1})	Band Assignment
3700-3400	OH stretching of Si-OH group
1643	OH stretching
1200-1000	Si-O-Si asymmetric stretching
750-800	Si-O-Si symmetric stretching
550-600	Si-O-Al stretching
485	Si-O-Fe stretching

D. Particle Size Analysis

The average particle size has been reduced from $94.5\text{ }\mu\text{m}$ to $0.70\text{ }\mu\text{m}$ shown in Table IV. There is a reduction of nearly 135 times in magnitude by this ball milling process.

TABLE IV
PARTICLE SIZE DISTRIBUTION

Samples	$D_{10}\text{ (}\mu\text{m)}^{\#}$	$D_{50}\text{ (}\mu\text{m)}^*$	$D_{90}\text{ (}\mu\text{m)}^{\times}$
Fresh FA	0.29	11.62	36.68
Sieved FA (-170# + 240#)	67.37	94.35	126.16
Ball milled FA	0.22	0.70	2.88

[#] $D_{10} = 0.29\text{ }\mu\text{m}$. 10% volume of the particles are less than $0.29\text{ }\mu\text{m}$ and remaining 90% are greater than $0.29\text{ }\mu\text{m}$ of fresh FA.

^{*} $D_{50} = 11.62\text{ }\mu\text{m}$. 50% volume of the particles are less than $11.62\text{ }\mu\text{m}$ and remaining 50% are greater than $11.62\text{ }\mu\text{m}$ of fresh FA.

[×] $D_{90} = 36.68\text{ }\mu\text{m}$. 90% volume of the particles are less than $36.68\text{ }\mu\text{m}$ and remaining 10% are greater than $36.68\text{ }\mu\text{m}$ of fresh FA.

IV. CONCLUSIONS

EDX analysis reveals that the FA used for this study belongs to class F. It was found that after 60 hrs of milling, crystallite size of quartz phase present in the FA was reduced from 37.58 nm to 9.25 nm and converts the surface into rough and reactive one. The average particle size has been reduced from $94.5\text{ }\mu\text{m}$ to $0.70\text{ }\mu\text{m}$ in which there is a reduction of nearly 135 times in magnitude, by this process. The anionic surfactant has played a vital role in reducing agglomeration of the FA particles. FTIR spectroscopy reveals that the characteristic -OH stretching vibration peak intensity increases by ball milling. The FA has become more amorphous and the crystallite size of the quartz phase has been reduced drastically. The spherical shape and smooth surface texture of the FA have been changed into irregular shape and rough surface by ball milling which is evidenced from TEM and SEM studies.

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