

Mechanical Activation of CaSO₄ Enriched Petroleum Coke Fly Ash for Development of Green Pellets

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Abstract: Mechanical Activation of calcium sulphate enriched petroleum coke fly ash (PCFA) generated from circulation fluidized bed combustion (CFBC) boiler was investigated to improve the surface reactivity of PCFA. The physico- chemical, mineralogical (XRD), morphological (SEM) characteristics of PCFA, activated PCFA and developed green pellets were studied in detail. It was found that the milling time of 45 minutes is efficient for the activation of PCFA and results in fragmentation of coarse particle into fine porous particles. Mechanical activation results in enhancing physical properties and reactivity of PCFA without any further chemical treatment. The mean particle size of activated PCFA with 45 min milling time was 12.51-12.60 μm and the porous morphology were seen through SEM. The hydration phases like ettringite, portlandite and calcium silicate hydrate mainly contribute to the development of mechanical strength in activated PCFA pellets which were also confirmed through morphology of needle-shaped crystallites. The study recommends that mechanically activated PCFA could be used as an adsorbent material for heavy metals removal from waste waters.

Keywords: Petroleum Coke Fly Ash; Grinding; Pellets; CFBC; Heavy Metals

1. Introduction: The rapid development of economics and industries have led to an upsurge in the release of toxic heavy metals such as Zinc, Nickel, Lead and Copper discharged into the environment resulting in significant environmental contamination and health issues to the human body for their non-biodegradable and persistent nature [1]. Removing these heavy metals from contaminated water has become critical. Various reported techniques were used to remove heavy metal ions from different types of wastewaters. Treatments based on adsorption, membranes, chemicals, electricity, and photo-catalysis can be made using these techniques. Adsorption is one of the more efficient and common techniques used for removal of heavy metal [2]. Many research has been done for the adsorption of toxic heavy metals from contaminated water using inexpensive adsorbents [3]. Fly ash is one of the most extensively researched materials for adsorption with solid wastes due to its affordability and easy availability [4]. Nevertheless, fly ash has a limited capacity to adsorb substances. Fly ash's capacity to

remove heavy metal ions from the environment can be improved by increasing its specific surface area [5,6].

Petroleum coke (Petcoke) is a by-product of the petroleum refining process, which is mainly used as primary fuel instead of coal due to its higher calorific value for power generation [7]. Petcoke fly ash (PCFA) is produced when sulfur-containing petcoke fuel is burned at 900°C in circulating fluidized bed combustion (CFBC) boilers utilizing limestone as a desulfurizing agent [8]. The chemical composition of ash, which significantly influences its activity, is reliant on the raw fuel mixture and the temperature at which combustion occurs. Desulphurization additives in CFBC boilers have an impact on the mineral and chemical content of the ash [9]. Although CFBC technology is efficient for combustion of low-grade fuel rich in calcium and sulphur [10,11] but due to the variation in their chemical compositions and having substantial amount of lime and SO₃, the use of CFBC ash in cement concrete system is limited [13-15]. The objective of this study is to investigate the use of PCFA for making green pellets. The

PCFA was mechanically activated using high energy planetary ball mill for enhancing the surface reactivity of PCFA for making economically and environment friendly green pellets which can be used for heavy metal adsorption in future studies. The raw PCFA, activated PCFA and pellets were analysed through X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Particle Size Distribution (PSD) to assess its suitability for its further application.

2. Material and Methods

2.1. Petroleum Coke Fly Ash: Fresh PCFA was collected from Electrostatic silos of Captive Power Plant of an Oil Refinery located in Madhya Pradesh which used petroleum coke as primary fuel. The industry used CFBC boiler for combustion of high calorific value sulphur rich petroleum coke and produced large quantities of ash around 5 million tons annually. The petroleum coke fly ash is produced at combustion temperature (800-900°C) and is calcium rich solid waste with value range between 40-50 wt%.

2.2. Mechanical Activation of PCFA: The activation of PCFA was done by grinding it in a high energy planetary ball mill (INSMART MRM-07) using 5 mm and 10 mm in a grinding jar of 500 mL capacity. PCFA was grinded for different milling time of 15, 30, 45 and 60 min at a bowl rotation speed (rpm) of 400 in 250 gram batches. The various parameters like sample to ball ratio and rotation speed were fixed and time was varied as per need. The efficiency of the grinding process in the ball mill reduced after 45 minutes of milling due to the material

agglomerating and adhering to the walls of the grinding jars and balls. Particle size analysis was performed with raw and milled ash samples using a Laser Scattering Particle Size Distribution Analyzer make Particle LA-950, HORIBA Scientific Northampton, UK.

2.3 Pelletization: The disc pelletizer used in the pelletization procedure has a diameter of 100 cm and a collar height of 15 cm. The disc is set at a fixed angle of 45° and rotates at a speed of 35 revolutions per minute. To begin with, the raw and milled ash were manually combined with a precisely measured quantity of water (water-to-solid ratio of 0.3) in order to achieve a uniformly mixed substance. The material is introduced into a disc, and additional water is applied via a spraying bottle as needed during the pelletization process. The disc continues till the appropriate size granules are achieved (Figure 1). The duration of one cycle is around 15 minutes. The prepared pellets were collected and allowed to undergo the curing process in an ambient condition for a duration of 7 days.

2.4. X-Ray Fluorescence Spectrometry Analysis of Pellet

The chemical composition of the raw ash was analysed using Wavelength- Dispersive X-Ray Fluorescence (WDX-XRF), S8 TIGER BRUKER, Germany.

2.5. X-Ray Diffraction Analysis of Pellet

The mineral composition of raw ash and milled ash pastes were determined by means of X-ray diffraction (XRD) analysis by Rigaku, Mini Flex II Desktop with $\text{Cu}\alpha$ ($\lambda=1.5419 \text{ \AA}$)

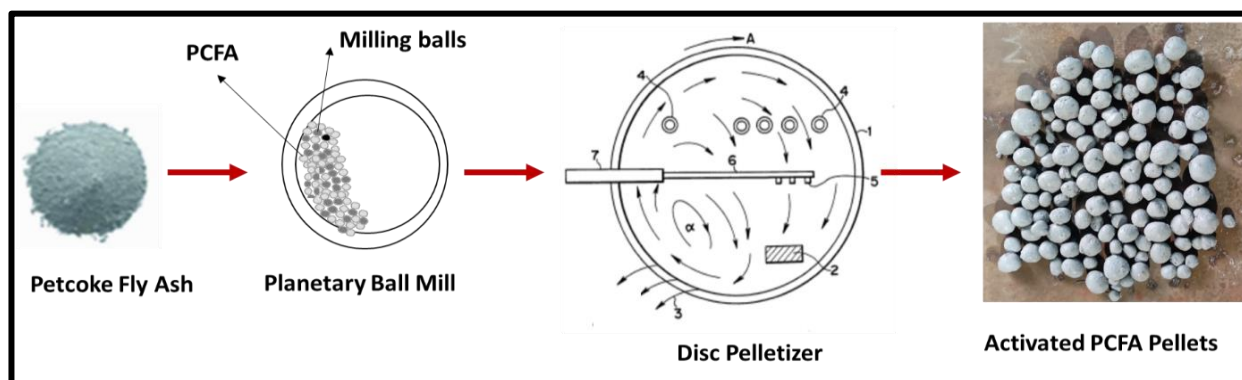


Figure 1. Schematic representation for preparation of green pellets through activated PCFA

radiation over the $10\text{--}70^\circ 2\theta$ region with step size of 0.02° and for approximately 30 min total scan time. The obtained peak was identified using JCPDS file.

2.6. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy Analysis

The Fourier Transform Infrared Spectroscopy (ATR-FTIR) patterns of raw ash and milled ash were measured by using Thermo Scientific, iS50 FT-IR. The IR spectra were obtained by measuring the transmittance of light in the range of $400\text{--}4000\text{ cm}^{-1}$, with a resolution of 4 cm^{-1} and 64 scans per sample.

2.7 Scanning Electron Microscopy Analysis

The microstructure was investigated using Scanning Electron Microscope JEOL JCM 6000 plus. In SEM, samples were investigated by making its surface conductive in high vacuum mode with deep gold coating. Samples were sprayed on carbon tape and then gold coated. Backscattered electron (BSE) images were obtained at $2000\times$ magnification, $10\mu\text{m}$ resolutions and 5 kV.

3. Results & Discussion

3.1. Particle Size Distribution of Raw and Activated PCFA: The particle size distribution pattern of raw PCFA and mechanically activated PCFA as a function of milling time are as shown in Figure 2. The particle size distribution was determined by Laser Scattering Particle Size Distribution Analyzer make ParticalLA- 950, HORIBA Scientific Northampton, UK. The raw PCFA is characterized by a particle size distribution with mean particle size of $16.79\text{--}19.23\ \mu\text{m}$ ($D_{10}\text{--}7.64\ \mu\text{m}$, $D_{50}\text{--}13.56\ \mu\text{m}$, $D_{90}\text{--}28.08\ \mu\text{m}$). In scanning electron microscope (SEM), the raw PCFA mainly comprise of coarse, angular and irregular particles with a broad particle size typically $< 50\ \mu\text{m}$ as shown in Figure 3(a). The material is dominated by irregular coarse particles of $5\text{--}20\ \mu\text{m}$. Few agglomerated particles are occasionally found typically ranging from $10\text{--}40\ \mu\text{m}$. The agglomeration of PCFA particles may be due to condensation and deposition of volatile

species [12,16] on the surfaces of PCFA. The grinding of PCFA in high energy planetary ball mill causes breaking up of larger particles of PCFA into sub-micron fine particles (Figure 3). The effective milling causes reduction in particle size with increase in milling time but after 45 mins of milling time larger particles start appearing due to agglomeration of particles as depicted in Table 1.

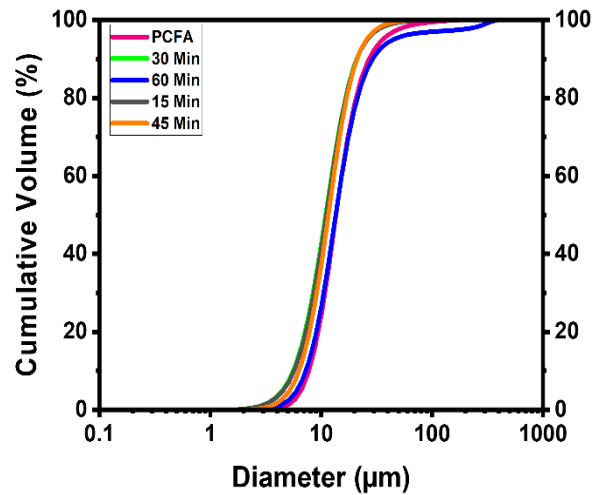


Figure 2. Particle Size Distribution Curve of the Raw PCFA and Activated PCFA

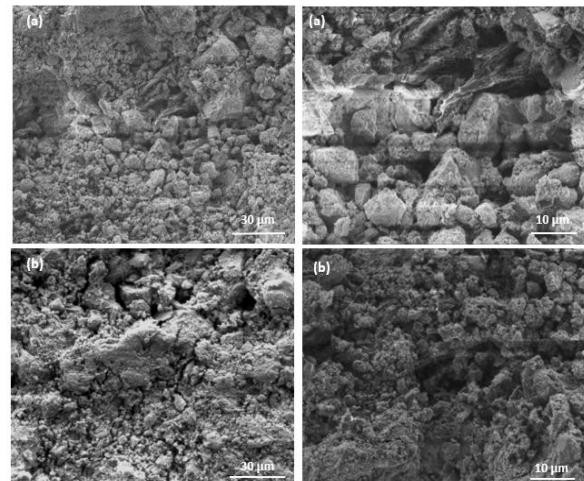


Figure 3. Scanning Electron Microscopy Images (a) Raw PCFA (b) Activated PCFA

The prolonged milling results in sticking of sample to the ball and to the surface of the container which further results in larger particle size than their primary particle due to agglomeration [17] which results in reduction of particle size decreases. The particles are so

Table 1: Grinding details of PCFA and its Particle Size Distribution

Sample: Ball	Time (in min)	RPM (Plate/Bowl)	Mean Size	D ₁₀	D ₉₀
1:2	15	200/400	20.3-23.12	7.24-7.36	28.4-29.2
1:2	30	200/400	12.12-13.06	5.5-6.29	19.9-21.2
1:2	45	200/400	12.51-12.60	5.57-6.01	19.9-20.9
1:2	60	200/400	12.51-12.78	5.6-6.1	20.0-21.13

fine that the electrostatic forces induce them to clump together [18]. These results are in accordance with the study reported by Fernández-Carrasco L [19] in which maximum size reduction fall in second stage grinding with milling time (30- 50 min). The mean particle size of activated ash for 30 min milling time is found to be 12.12-13.06 μm (D10- 5.895 μm and D90- 20.55 μm) which results in internal porosity of the particle which may also be confirmed through SEM morphology (Figure 3(b)).

3.2. Chemical Composition of the Raw and Activated PCFA: The primary chemical components of raw PCFA and activated PCFA are predominantly CaO and SO₃, with an average value of 45.95 and 28.1 weight%, respectively (Table 2). The average content of SiO₂, MgO Al₂O₃, Fe₂O₃ and V₂O₅ in raw ash is 10.5, 4.0, 2.65, 0.7 and 0.08 wt% respectively. Like other CFBC ashes, PCFA exhibits a significant concentration of sulphur, specifically in the form of SO₃, which is a result of the desulphurization process in the

CFBC boiler.

3.3. Phase composition and microstructure of Pellets:

The raw and activated PCFA based pellets were crushed and finely powdered manually using mortar and pestle & passed through sieve number 200 (75μm). The prepared powder sample was tested for hydration phase analysis using X-ray diffraction. The resultant intensity peaks were confirmed through JCPDS files. The mineral phases of the pellet derived from raw and activated PCFA (Figure 4) exhibit notable distinctions from the mineral phases of the raw ash PCFA. The differences arise from a sequence of hydration reactions. The main hydration peak found in both the samples were portlandite and calcium silicate hydrate and ettringite. The main peaks of ettringite were found at (2θ-17.0°, 17.8°, 11.4° and 35.8°) (JCPDS- 9-414) and peaks of calcium silicate hydrate were found at (2θ- 32.0°, 39.2° and 27.3°) (JCPDS- 29-368). The presence of the gypsum phase indicates the dissolution of anhydrite in hydrated pastes at (2θ- 30.9°, 20.5°

Table 2: Chemical Composition of Raw and Activated PCFA, * LOI - Loss on ignition at 900 °C.

Metal Oxide (in wgt %)	CaO	SO ₃	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	V ₂ O ₅	LOI
PCFA	46.1	28.2	10.8	4.07	2.62	0.78	0.54	0.12	0.086	8.99
Activated PCFA	45.8	28.0	10.3	4.06	2.60	0.75	0.54	0.13	0.085	9.06

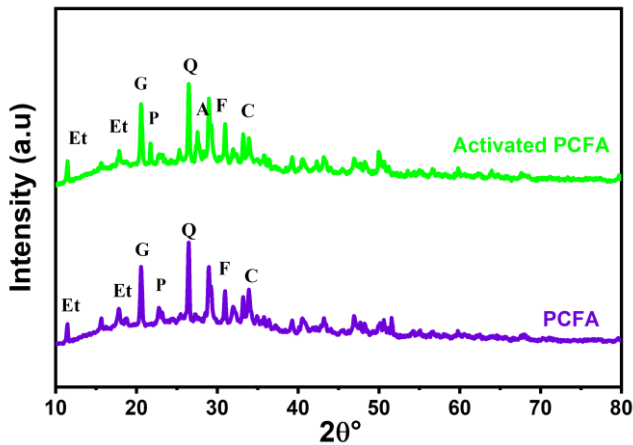


Figure 4. XRD Patterns (a) PCFA based Pellets; (b) Activated PCFA based Pellets (P: Portlandite; A: Anorthite; Et: Ettringite; F: Iron Vanadium Oxide; G: Gypsum; C: Calcium Silicate Hydrate; Q: Quartz

and 33.2°) (JCPDS-21-816). ATR-FTIR spectra of pellet from raw PCFA and activated PCFA are shown in Figure 5. The molecular bonds produce narrow peaks in highly crystalline structures; wider peaks show an amorphous structure. The prominent and well-defined peaks observed at approximately 1096 and 1112 cm^{-1} in PCFA and activated ash, respectively, as well as the moderately intense but distinguishable peaks at 594 , 611 , and 676 cm^{-1} in PCFA and at 594 , 611 , and 677 cm^{-1} in activated PCFA can be attributed to the bending and stretching vibrations of the S-O bonds in the SO_4^{2-} ions present in the Calcium Sulphate Anhydride mineral. Such effects indicate the presence of anhydrite [20]. The characteristic band at 2933 cm^{-1} in PCFA and BA corresponds to the vibration mode of C-H. Sharp visible band at 3642 cm^{-1} in activated PCFA is due to the vibration of O-H in portlandite ($\text{Ca}(\text{OH})_2$) compound. A moderate intense band at an extreme value of 1411 cm^{-1} , 1457 cm^{-1} represents C-O stretching, band at 873 cm^{-1} and 874 cm^{-1} corresponding C-O out of plane band. The observed effects suggest the presence of calcite (CaCO_3) in PCFA and activated PCFA, as indicated by the respective changes. Additionally, the band at around 1620 cm^{-1} corresponds to the stretching vibrations of O-H bonds of water molecules. The presence of an additional distinct peak at 797 cm^{-1} in the activated sample matches to the vibrational frequency of the Si-O bond in

Quartz [21]. The above FTIR results confirmed the hydration of lime to portlandite ($\text{Ca}(\text{OH})_2$) in pellet sample with activated ash with the presence of band at 1620 cm^{-1} & 3642 cm^{-1} which may also be confirmed through the XRD pattern.

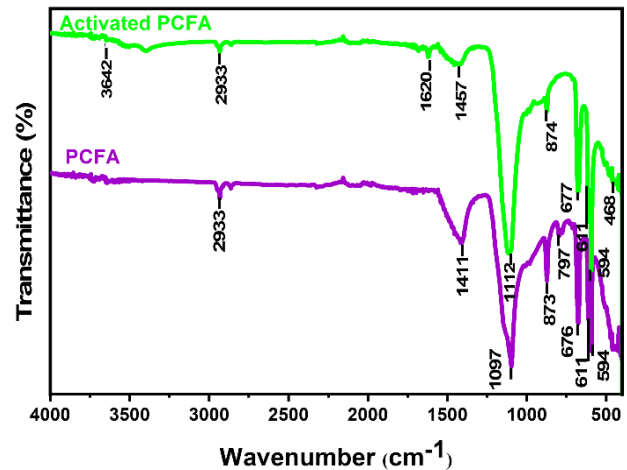


Figure 5. Fourier Transformation Infrared Spectra of PCFA and activated PCFA based Pellets

The SEM analysis of pellet from raw PCFA and activated PCFA shows a porous structure with substantial pore space partially filled with hexagonal shaped portlandite crystals (Figure 6(A)(B)).

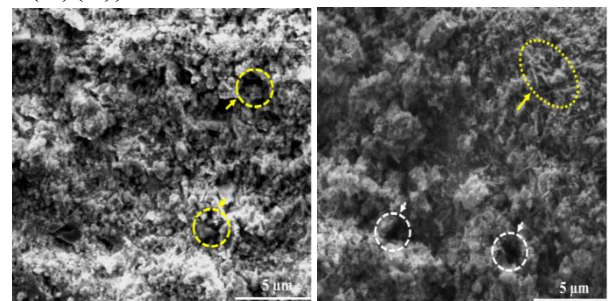


Figure 6. SEM Image (A) PCFA based Pellet (B) Activated PCFA based Pellets

The microstructure of pellets containing mechanically activated PCFA slightly differ from those containing PCFA alone. It exhibits a distinct morphology characterized by needle-shaped crystallites of ettringite, which are submicron in size (Figure 6B). The SEM image of activated ash pellets also confirms the hydration reaction between the water and PCFA the clear spiky and elongated microstructure of calcium silicate hydrate. The production of ettringite and calcium silicate

filled the pores and increased specimen compaction [22]. It was confirmed that the lime (CaO) in PCFA and activated PCFA get converted into portlandite (Ca(OH)₂) by mean of hydration reaction and used for the formation of C-S-H and Ettringite [23].

4. Conclusions:

- The mean particle of size of raw PCFA is 16.79-19.23 μm (D10-7.64 μm, D90-28.08 μm) and the mean particle size of activated PCFA (45 min) is 12.51-12.60 μm (D10-5.57 μm D90-19.9 μm).
- The mechanical activation of 45 minutes is efficient for the activation of PCFA which enables the fragmentation of coarse particles and results in improving the surface reactivity and physical properties which is confirmed through particle size distribution.
- The XRD & FTIR analysis confirms the hydration reaction of CaO and CaSO₄ which get converted into portlandite, calcium silicate hydrate and ettringite phases which are mainly contributing in mechanical strength development in PCFA pellets.
- The microstructure of mechanical activated PCFA based pellet confirmed the formation of needle shaped ettringite that occupied the pore space between unreacted particles and hence improve the mechanical strength.
- The findings of the study suggest that mechanically activated PCFA could be used as an adsorbent material for adsorption of heavy metal and also as an alternative binder.

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Supervision: [Mohd. Akram Khan].

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