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Microstructural and Mineralogical Properties of Acid and Alkali Activated Coal Fly Ash

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ABSTRACT

Fly ash (FA), a coal combustion residue of thermal power plants has been regarded as a problematic solid waste all over the world. In this study FA samples were modified with NaOH and H₂SO₄. The mineralogical and microstructural characterization were carried out by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) and Braunauer-Emmett-Teller's multilayer adsorption theory (BET). Experimental data showed that cenospheres were dominated with quartz and mullite glasses with both amorphous and crystalline phases. The acid treatment increased Si/Al ratios by removing impurities and dealuminations but alkali treatment significantly increased total pore volume. The specific surface area of alkali and acid treated samples were found 6.9 m²g⁻¹ and 2.1 m²g⁻¹ respectively, while that of virgin material was 1.5 m²g⁻¹.

1. Introduction

Coal fly ash is an industrial waste generated from coal combustion process in thermal power plants. Presently worldwide more than 750 million tons of fly ash is produced per year and it will reach around 13.33 billion tons by the year 2030 [1]. Only about 10-30 percent of it is used mainly as an additive in cement concrete, structural fills etc. The rest has to be stored in ponds or deposited in old mines, which causes air, water and soil pollution.

The particle size of fly ash is 0.5 to 100 μm with fine glassy powder and generally spherical shape. It is classified into two types according to the type of coal used. Class F fly ash is produced by burning of anthracite and bituminous coal. On the other hand, lignite or sub-bituminous coal produces class C fly ash which has self-cementing properties [2].

Fly ash is a fine powdered ferroaluminosilicate material containing Al, Ca, Mg, Fe, Na and Si as the predominant elements. Some toxic metals such as Cr, As, Hg, Ni, V, Pb, Zn and Se also found in it. It is a complex heterogeneous mixture of both amorphous and crystalline phases [3].

The alkali activation of fly ash produces N-A-S-H gel (Na₂O-Al₂O₃-SiO₂-H₂O) by sharing O atoms in order to create a three-dimensional framework of SiO₄ and AlO₄ tetrahedral link [4-6].

Treatment with H₂SO₄ enables the removal of impurities (i.e., Fe₂O₃, TiO₂, MgO, CaO, K₂O and Na₂O) in FA resulting in the presence of higher SiO₂ and Al₂O₃ percentages in the product. The treatment provides the highest purity raw material (70-77% of SiO₂ and Al₂O₃ depending on the acid concentration) [7]. Chemical activation using H₂SO₄ increases the H⁺ ion content within the fly ash producing active H-fly ash cluster which releases proton easily and thus it would act as a Bronsted acid cluster. After activation using H₂SO₄ with concentration 9 M, Si and Ti compound had improved to 47.70% and 2.49% while Fe compound was decreasing upto 29.40% [8].

The objective of the present study was to investigate the chemical, mineralogical and structural composition of the fly ash and the effect of modification in order to find out a possibility of an economically efficient use and reduce the environment pollution.

2. Experimental Methods

2.1 Materials

The material used in this work was coal fly ash from Barapukuria Thermal Power Plant (BTTP) which is the coal-based power plant in Bangladesh established beside Barapukuria Coal Mine Co. Ltd.

2.2 Alkali and Acid Activation of Fly Ash

The untreated fly ash (UFA) was activated by refluxing with 5 M NaOH and 5 M H₂SO₄ solution. The products used to prepare the solutions were laboratory grade reagents: 98% sodium hydroxide (NaOH) pellets supplied by Merck KGaA, Germany and 98% sulphuric acid (H₂SO₄) supplied by Loba Chemie pvt. Ltd. 107, India. 20 g fly ash was taken in a round bottom flask with 200 mL alkali/ acid solution to reflux for 4 h at 120 °C. The resulting suspended was filtered and washed with deionized water to reach pH nearby 7. The obtained solid products were dried at 120 °C overnight and calcined at 550 °C for 4 h under static condition in a muffle furnace. These treated samples were denoted as BFA (base treated fly ash) and AFA (acid treated fly ash).

2.3 Characterization Techniques

The characterization of fly ash samples were carried out with a number of experimental approaches in order to investigate all the relevant features present in the samples. The FTIR spectra were measured using 8400S SHIMADZU, Japan infrared spectrophotometer from 4000 to 400 cm⁻¹, with a resolution of 2 cm⁻¹. The KBr pellet method was used to prepare the samples. Powder X-ray diffraction studies were carried out by using (X'Pert-PRO XRD) analytical diffractometer with monochromatic CuKα radiation (λ = 1.54056 Å) in a 2θ range of 20-65°. A scanning electron microscope (SEM) (model-JEOL-JSM-7600F) with energy dispersive spectroscopy (EDS) was used to evaluate the texture, morphology and elemental composition of samples. The BET surface area was measured by N₂ adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using BELSORP MINI-11(BEL JAPAN) surface area analyzer. The analysis procedure was automated and operates with the Belsorp adsorption/desorption data analysis software-Ver.6.1.0.8. Before each measurement, the sample was out gassed first at 165 °C for 1.5 hours, under N₂ gas flow.

3. Results and Discussion

3.1 XRD Analysis

The X-ray diffraction patterns of untreated and treated fly ash are shown in Fig. 1. This pattern of UFA indicated that the major mineral phases in fly ash were quartz, mullite and hematite together with crystalline and amorphous component. The UFA showed a broad gibbosity in the range 2θ value 20-35° because of having amorphous components, which increased after alkali activation, but decreased after acid activation. The peaks at 26.2°, 42.6°, 39.2°, and 63.6° showed mullite (aluminosilicate) phases, while quartz (silica) exhibited strong peaks at 20.7°, 26.6°,

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40.9°, 49.5° and 54.1° of 2θ values. This finding is consistent with Tanka's and Chisholm's finding [9-11]. Peaks at 37.1° and 35.2° indicated lime and iron oxide [12] respectively, which was also confirmable with EDS analysis.

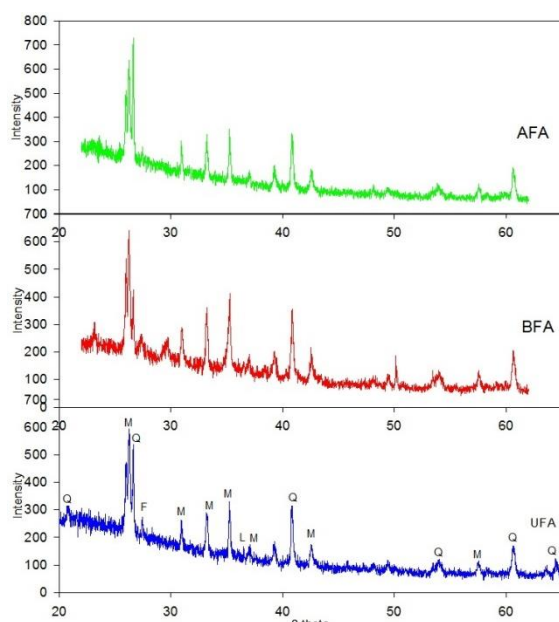
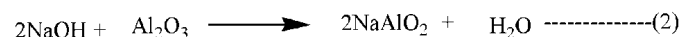
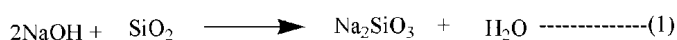
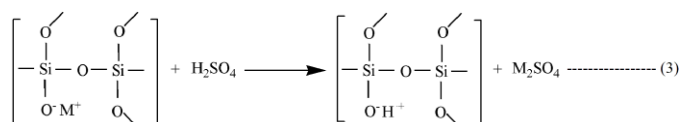


Fig. 1 XRD patterns of samples

This result suggested that BFA and AFA had almost similar XRD patterns; the major crystalline phases in the treated fly ashes were found to be quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) with small quantities of magnetite and hematite [13]. Two new peaks at 29.7° and 50.2° were observed after alkali activation because of formation of silicate and aluminate by the following reactions:



The characteristic peaks of quartz in the AFA were more concentrated which indicated the increment of SiO_2 percentage. Acid treatment of fly ash removed some elements like Na, Mg and other oxides located mainly in the outer part of the particles by the following cation exchange reaction:



3.2 FTIR Studies

The FT-IR spectra of raw and activated fly ash are shown in Fig. 2. The UFA showed two noticeable strong bands because of the internal vibrations of tetrahedral TO_4 ($\text{T}=\text{Al}, \text{Si}$). One of them was at around 1093 cm^{-1} , associated with T-O bond asymmetric stretching vibrations (this band provides information on the degree of crystallinity of a sample), while the other, centered at 460 cm^{-1} , corresponded to T-O bond internal deformation vibrations.

A series of bands located at 1139, 1051, 788–740, 669, 543 and 462 cm^{-1} were due to the presence of quartz and another at around 1139–1112 cm^{-1} and 543 cm^{-1} (band associated with the octahedral aluminium present in mullite) [14, 16].

Two new components appearing at around 1143 and 685 cm^{-1} were attributed to the sodium aluminosilicate gel formed as a result of alkali activation. Finally, the presence of the band at 1166–1130 cm^{-1} was regarded to both quartz and mullite. Bands from 800–500 cm^{-1} correspond to the vibrations of external ring which formed in silicates and aluminosilicates, when the AlO_4 and SiO_4 tetrahedral were linked by oxygen atoms [16, 17].

IR spectrum of acid treated fly ash shows sharp and high intense band at 1099 cm^{-1} which was attributed to the modes of Si-O-Si asymmetric band stretching vibrations compared to others (UFA and BFA). It indicated the distinct nature of acid treatment by the removal of impurity mineral phases from FA and produced pure crystalline faujasite [18, 19].

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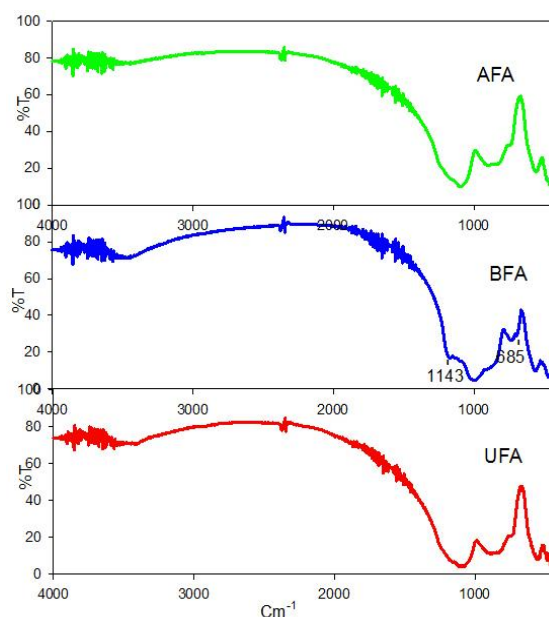


Fig. 2 FT-IR spectra of samples

3.3 SEM-EDS

In order to identify and characterize the mineral phases and morphology, SEM is one of the best and most widely used techniques. Fig. 3 shows the SEM image of raw and modified samples. The SEM image of raw sample as shown in Fig. 3(a) indicated many spherical particles along with irregular shapes. The rounded particles with a wide distribution in size were predominantly glassy and mostly comprised of crystalline solids such as quartz, mullite, magnetite and hematite.

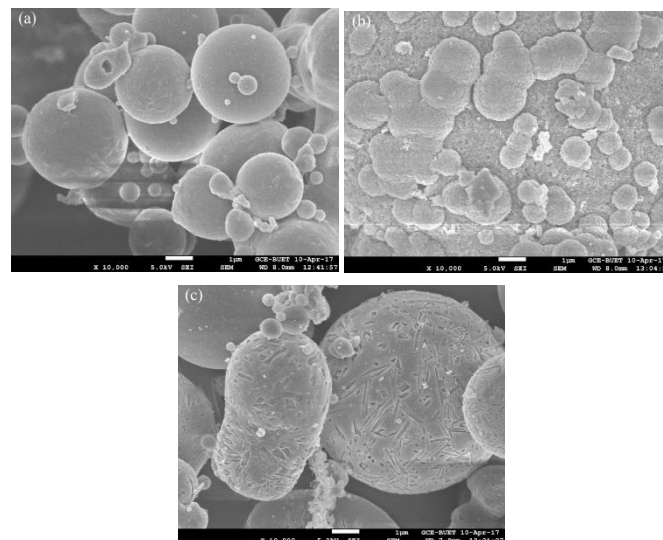


Fig. 3 SEM microphotograph of (a) UFA (b) BFA (c) AFA

The crystalline and spherical particles turned into agglomerated phase [18] after alkali activation as shown in Fig. 3(b). H_2SO_4 being a very corrosive acid, treatment of the material with this acid was likely to erode the surface and create a porous structure with uneven topography as shown in Fig. 3(c).

The elemental composition of ash samples was determined and confirmed by EDS as shown in Table 1. All the samples were predominantly contained oxygen, aluminium and silicon. The identified elements in the fly ash samples were O, Al, Si, Ti, Fe in various compounds (SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 etc.) as determined by EDS. This indicated that the ratio of Si/Al increases because of dealumination if leached with strong acid.

Table 1 Elemental composition (weight %) of fresh and modified fly ash

	Si:Al	O	Na	Mg	Al	Si	S	Ca	Ti	Pb
UFA	0.84	39.92	0.10	0.04	11.35	9.55	0.10	0.20	0.30	0.73
BFA	0.57	44.18	5.26	0.24	21.43	12.30	0.34	0.74	3.06	2.1
AFA	1.06	31.36	-	-	26.66	28.19	0.11	-	0.19	0.94

3.4 Textural Parameters

The textural properties of the materials are shown in Table 2. Adsorption/desorption isotherm of N₂ for fly ash represented II type (according to IUPAC recommendations) with a hysteresis loop of type H3, normally attributed to porous solids with capillary condensation occurring inside the micropores [20, 21]. Significant difference was observed for the alkali treated sample. It needed about twenty-five times higher absorbed in the same relative pressure range comparing with untreated sample; this was because of remarkable increasing of total pore volume as well as surface area as shown in Fig. 4.

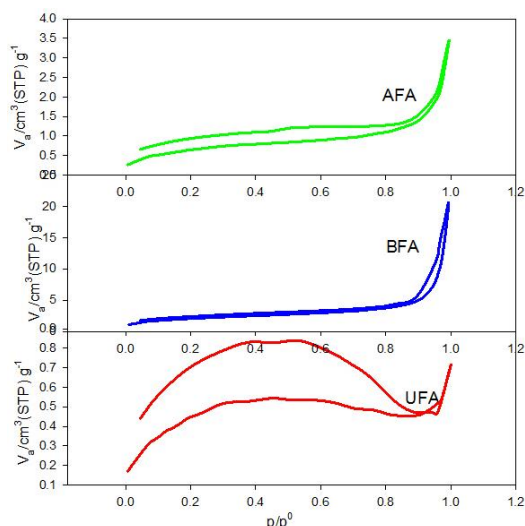


Fig. 4 Adsorption/desorption isotherm of N₂ (-196.15 °C)

Specific surface area calculated by the BET method increased significantly after the alkali treatment because of the texture of micropores of zeolitic structure [22, 23]. The specific surface area of BFA material was 6.9 m²g⁻¹, which was slightly larger than AFA (2.1 m²g⁻¹).

Table 2 Physical characteristics of fresh and modified fly ash

Materials	BET specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mean pore diameter from BJH plot (nm)
UFA	1.5	0.10×10 ⁻²	1.42
BFA	6.9	2.91×10 ⁻²	1.42
AFA	2.1	0.50×10 ⁻²	1.42

Pore size distribution (PSD) determined on the basis of BJH calculation (Barrett-Joyner-Halenda method) is presented in Fig. 5. It could be observed from the PSD that the alkali treatment affected much comparing with that of acid treatment.

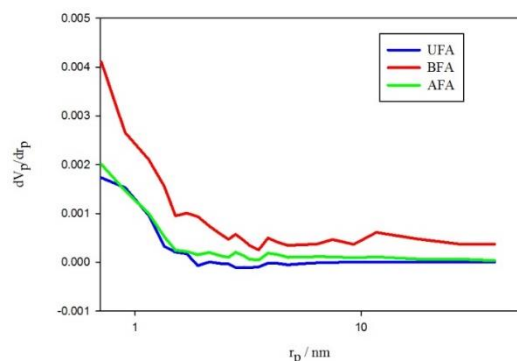


Fig. 5 BJH desorption pore size distributions (nm)

4. Conclusion

Fly ash can be considered as hazardous solid waste because of its disposal problem. The major chemical components in the fly ash were SiO₂ and highlighting the aluminosilicate nature of the starting material and the availability of Si and Al necessary for geopolymer formation. The fly ash consisted of smooth aluminosilicate spherical particles, while the

morphology of the BFA featured agglomerated and irregular particles, thus showing the extent to which the cenospheres were attacked by the hydroxide component and increased surface area. Having high pore volume and specific surface area, alkali leached fly ash can be used for further utilizations, such as water treatment, cement concrete additives etc.

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References

- [1] R. Islam, M. Hasan, R. Karim, M.F.M. Zain, Properties of fly ash brick prepared in local environment of Bangladesh, *Int. J. Civ. Environ. Struc. Cons. Arch. Eng.* 9 (2015) 1533-1537.
- [2] S.V. Vassilev, C.G. Vassileva, A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behavior, *Fuel* 86 (2007) 1490-1512.
- [3] A. Dwivedi, M.K. Jain, Fly ash – waste management and overview: A review, *Recent Res. Sci. Technol.* 6(1) (2014) 30-35.
- [4] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes, *Cem. Concr. Res.* 29 (1999) 1323-1329.
- [5] Y. Ma, J. Hu, G. Ye, The pore structure and permeability of alkali activated fly ash, *Fuel* 104 (2013) 771-780.
- [6] M. Criado, W. Aperador, I. Sobrados, Microstructural and mechanical properties of alkali activated colombian raw materials, *Mater.* 9 (2016) 158-1-16.
- [7] P. Panitchakarn, T. Klamrassamee, N. Laosiripojana, N. Viriya-empikul, P. Pavasant, Synthesis and testing of zeolite from industrial-waste coal fly ash as sorbent for water adsorption from ethanol solution, *Eng. J.* 18(1) (2014) 1-12.
- [8] A. Ghofur, Atikah, Soemarno, A. Hadi, Characterization of coal fly ash as converter catalytic material in reducing Hc And Co exhaust gas from motor vehicles, *J. Environ. Sci. Toxi. Food. Technol.* 9(9) (2015) 12-16.
- [9] A. Sharma, S. Kabra, S. Katara, A. Rani, Variation of surface morphology and physico-chemical properties of the fly ash through mechanical and thermal activations, *J. Adv. Chem. Sci.* 1(2) (2015) 70-74.
- [10] H. Tanaka, S. Matsumura, S. Furusawa, R. Hino, Conversion of coal fly ash to NaX zeolites, *J. Mat. Sci. Let.* 22(4) (2003) 323-325.
- [11] J. Chisholm, Comparison of quartz standards for X-ray diffraction analysis: HSE A9950 (Sikron F600) and NIST SRM 1878, *Ann. Occup. Hyg.* 49(4) (2005) 351-358.
- [12] T.P. Amaladhas, S.S. Thavamani, Synthesis, characterization and catalytic activity of transition metal complexes of ascorbic acid encapsulated in fly ash based zeolite, *Adv. Mat. Lett.* 4(9) (2013) 688-695.
- [13] A. Sarkar, R. Rano, G. Udaybhanu, A.K. Basu, A Comprehensive Characterization of Fly Ash from a Thermal Power Plant in Eastern India, *Fuel. Proce. Technol.* 87 (2006) 259-277.
- [14] J. Temuujin, K. Okada, K.J.D. Mackenzie, Effect of mechanochemical treatment on the crystallization behaviour of diphasic mullite gel, *Ceram. Int.* 25 (1999) 85-90.
- [15] A. Tinti, V. Tugnoli, S. Bonora, O. Francioso, Recent applications of vibrational mid-Infrared (IR) spectroscopy for studying soil components: a review, *J. Cent. Europ. Agri.* 16(1) (2015) 1-22.
- [16] M. Criado, A.F. Jimenez, A. Palomo, Alkali activation of fly ash: Effect of the SiO₂/Na₂O ratio: Part I: FTIR study, *Micro. Meso. Mater.* 106 (2007) 180-191.
- [17] B.K. Singh, N. Pragya, Characterization of various flyash fractions for adsorption processes, *Res. J. Mater. Sci.* 3(3) (2015) 7-16.
- [18] N.L. Subbulekshmi, E. Subramanian, New synthesis process of crystalline phase - pure faujasite zeolite material from sialic type coal fly ash, *J. Adv. Chem. Sci.* 2(2) (2016) 284-288.
- [19] J.J. Clara, P.K. Sugirtha, Study of SEM/EDXS and FTIR for fly ash to determine the chemical changes of ash in marine environment, *Int. J. Sci. Res.* 5(7) (2016) 1688-1693.
- [20] M. Thommes, Physical adsorption characterization of nanoporous materials, *J. Chem. Eng. Tech.* 82(7) (2010) 1059-1073.
- [21] M. Wdowin, M. Franus, R. Panek, L. Badura, W. Franus, Erratum to: The conversion technology of fly ash into zeolites, *Clean. Technol. Environ. Policy.* 16 (2014) 1217-1223.
- [22] W. Franus, Characterization of X-type zeolite prepared from coal fly ash, *Pol. J. Environ. Stud.* 21(2) (2012) 337-343.
- [23] W. Franus, M. Wdowin, M. Franus, Synthesis and characterization of zeolites prepared from industrial fly ash, *Environ. Monit. Assess.* 186(9) (2014) 5721-5729.