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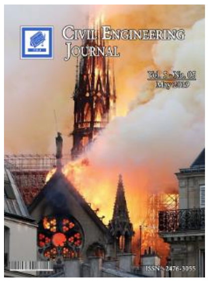

Physiochemical Characterization and Dematerialization of Coal Class F Flyash Residues from Thermal Power Plant

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Abstract

Class F flyash has a low percentage content of lime and is considered as a leading category of flyash generated in India with an average utilization of nearly 55% of flyash produced by the coal-burning power plant. The coal Class F flyash residue sample has been collected from Harduaganj, Thermal Power Station India. The paper illustrates the outcome of the study carried out to examine all the relevant features of the chemical and physical properties of Class F flyash sample. Elementary quantitative results from point analysis, SEM/EDS, FTIR, and pH analysis have been done in the chemical analysis of the study. The physical characterization of the sample is done by several experimental approaches to compare all the relevant features of Class F flyash sample and common soil. The main objective of this study is to evaluate whether the locally available Class F flyash from Harduaganj Thermal Power Station India, will provide satisfactory performance in fully or partially replacement of common soil. The performance evaluation of flyash and soil in different test results included bulk density, specific gravity, plasticity, maximum dry density, optimum moisture content, and permeability in accordance with the relevant IS or ASTM standards. Finally, the reported research recommended the selection of Class F flyash sample with low-lime content that provided the close correlation of its physical properties to the common soil.

Keywords: Flyash; Class F; Class C; Utilization; Chemical; Physical; SEM/EDS.

1. Introduction

All over the world the coal based thermal power plant is one of the most effective resources for the production of electricity. A large variety of secondary materials are produced due to this process. Any material that are generated from coal-combustion processes are referred as a Coal-Combustion Product (CCP). Flyash is considered as one of the most widespread produced CCP among all possible types of CCPs that are generated at coal-burning power plants worldwide. The characterization of flyash can be discussed as the fine fraction of coal ash that exits in the combustion chamber of flue gas and is detained by air pollution control equipment at electric power plants [1]. From the shape point of view, the flyash are usually spherical and they solidify when in suspension form in exhaust gases. Flyash is generally composed of silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3).

The chemical and physical characteristics of flyash vary typically on its anticipated utilization. Therefore, the particular needs for the use of flyash in soil stabilization or concrete are discussed in detail in references [2, 3]. According to the classification [2], flyash is classified into two classes' viz. Class F and Class C. The content of silica, calcium,

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iron and alumina in the ash is the major difference between these classes. The chemical characteristics of flyash samples are basically influenced by the chemical content of the coal burned (i.e., bituminous, anthracite, and lignite). The burning of older and harder anthracite and bituminous coal produces Class F flyash. The flyash so produced is pozzolanic in character and possess less than 10% lime, (CaO). The alumina and glassy silica of Class F flyash needs Portland cement, quicklime or hydrated lime as a cementing agent and in the presence of water it reacts and produces cementitious compounds. An alternate method is the addition of a chemical activator to Class F flyash like sodium silicate (water glass) that may lead to the formation of geopolymer. The combustion of younger sub-bituminous coal or lignite may generate flyash with pozzolanic properties and self-cementing properties. Class C flyash is known to harden in presence of water and gains strength over prolonged period. Class C flyash usually possess more than 20% lime (CaO). Class C with self-cementing property does not need an activator, unlike Class F. Alkali and sulfate (SO_4) amount are generally higher in Class C flyash. The aim of this investigation is to characterize the various chemical and physical properties of Class F flyash which discovers its potential utility. For this purpose; flyash is characterized with respect to its physical and chemical properties to look for the utilization of Class F flyash as resource material in construction industry.

1.1. Current Scenario of Flyash in India

In the world rank of coal and coal-based thermal power plants, India is the third largest producer which contributes to about 70% of the total installed capacity for generation of power [4]. Though, over 40% ash content produced by bituminous and sub-bituminous coal. There are 120 known coal-based thermal power plants existing in India which on an average generate 120-160 million tons of coal flyash [5]. The emerging amount of average generation and utilization data received during the last five years by Environmental Information Centre (ENVIS) on flyash is 166 million tons and 96 million tons [5]. The flyash generation and utilization in India during the year 2011-12, 2012-13, 2013-14, and 2014-15 and 2015-16 are shown in Table 1.

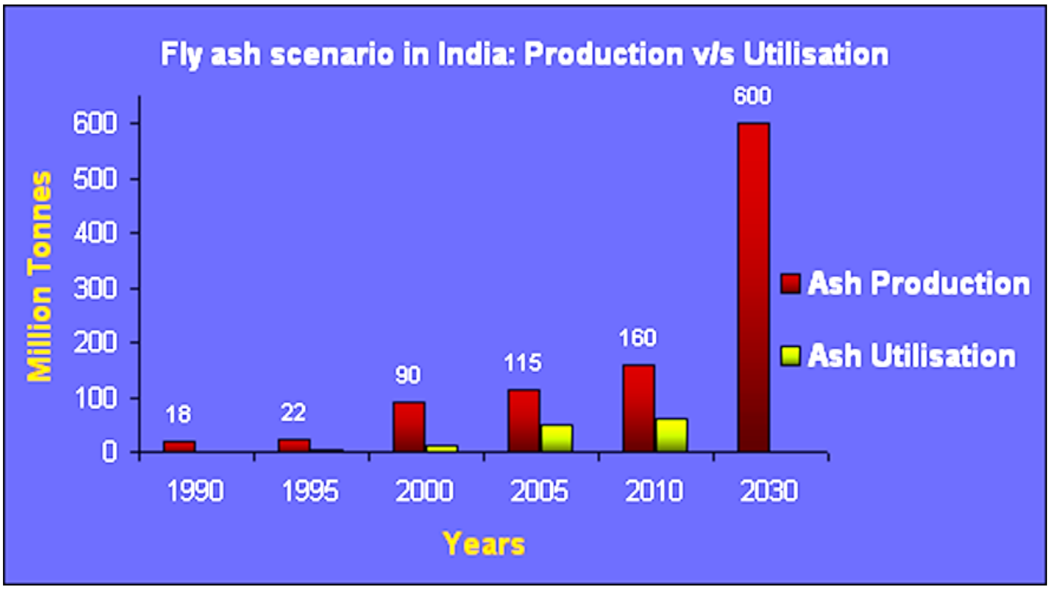
Table 1. Current status of flyash generation and utilization in India

Description	2011- 12	2012-13	2013-14	2014-15	1st Half Year 2015-16
Number of thermal power stations in India from which data was received	124	138	143	145	132
Installed capacity (MW)	1,05,925.3	1,20312.30	1,33,381.30	1,38,915.80	1,30,428.80
Coal consumed (million tons)	437.41	482.97	523.52	549.72	251.69
Average ash content (%)	33.24	33.87	33.02	33.50	33.23
Flyash generation (million tons)	145.42	163.56	172.87	184.14	83.64
Flyash utilisation (million tons)	85.05	100.37	99.62	102.54	46.87
Percentage utilization	58.48	61.37	57.63	55.69	56.04

Source:ENVIS Centre on Flyash Hosted by CSIR-Central Building Research Institute, Roorkee

Sponsored by Ministry of Environment, Forests & Climate Change, Govt. of India

Flyash generation and utilization data for the first half of 2015-16 (April, 2015 to Sept., 2015) has been received from 132 coal/lignite-based thermal power stations of different power utilities in India. The data received as on 15th March, 2016 has been investigated to obtain conclusions on the present known status of flyash generation and its utilization in India as a whole [6]. Flyash utilization percentage (of 146 thermal power stations) has increased during the first half of 2015-16 in comparison to the utilization during the first half of the previous year 2014-15[6]. ENVIS centre on flyash hosted by CSIR-Central Building Research Institute, Roorkee sponsored by Ministry of Environment, Forests and Climate Change, Government of India also shows the correlation in production and utilization of flyash from 1990 to expected 2030. The flyash generation and utilization scenario in India from 1990 to 2030 is represented in Figure 1.



Source:ENVIS Centre on Flyash Hosted by CSIR-Central Building Research Institute, Roorkee

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Figure 1. Current flyash scenario generation vs utilization

1.2. Published Studies on Class F Flyash

The incorporation of the supplementary cementation materials like flyash and kaolin in the concrete mix may produce High Performance Concrete (HPC) [7]. The fibre reinforced flyash with lime stone dust brick (10FRFALSDB3') possessed the highest compressive strength of 9.155 MPa with 10% stone dust and 10% cement [8, 9]. After experimental tests on Class F flyash-based brick tiles, it is being concluded that tiles showed poor performance at lower compressive strength as compared to the conventional clay roof tiles. The study [10] shows that on increasing the percentage of Cement (C) at the fixed percentage of Treated Flyash (T.F.A) and Radish Stone Dust (R.S.D), the lower permeability values were found. Though permeability (k) falls sharply with the variation of Coarse Sand (C.S) with C, the value of k has been found in the range of 10^{-7} (closer to the value of clay available in the market for making bricks and roof tiles). Through new sets of experiment conducted by [11], its compressive strength increased to 30.65% as compared to the previous studies carried out by [9-11]. The study suggested that the flyash-scrap tire fiber composite offers a sustainable supplement to the traditional insulation which increases the efficiency of traditional insulation as well as help in reducing the percentage of disposed waste products [12].

The literature survey has established flyash as air and water pollution source. This resource may act as a material in construction industry, thereby approaching to a clean management of environment. Till a decade back, flyash was treated as waste material worldwide, but now it is developed as an environment saviour [13]. Various methods are suggested to use flyash, such as in the construction industry, agriculture, waste water treatment and management of environmental pollution [14].The replacement of cement by flyash in concrete has resulted in the reduction of total voids, which may be attributed to the micro-filler effect of flyash. Consequently, there is a reduction of about 13.28% in permeability of pervious flyash–cement concrete [15].The current annual worldwide production of coal ash is estimated about 700 million tons of which 70% is flyash at least and based on the more references, flyash can be used in different areas of building engineering thanks to its appropriate characteristics. It is obvious that the type of combusted coal has the significant impact on the chemical, physical and mineralogical characteristics of the flyash and its further utilization [16, 17]. The present study evaluates the application of class F flyash as a partial replacement of binder in concrete. The compressive strength of the fly ash samples showed low early compressive strength comparing to the control samples. However, due to pozzolanic reaction strength was improved gradually over a longer period of time, whereas control samples stopped the strength growth after 56 days of curing.

2. Materials and Methods

The flyash was obtained from Harduaganj, Thermal Power Station Aligarh, Uttar Pradesh India. The flyash was dried at 110°C in an electric oven for 2 h and stored in a desiccator for studying chemical and physical studies. For the comparison of physical properties, the sample of common soil was taken from the construction site of Sharda Mall Aligarh, India. Class F flyash sample was used after pretreatment with calcium hydroxide that enhances the cementitious properties of flyash sample. The sample's surface morphology was analysed using JEOL JSM-6510LV Scanning Electron Microscope (SEM) assisted with Energy-Dispersive X-ray spectroscopy (EDX). EDS was used to characterize the samples in this study. The elemental analysis of the sample was done in "spot mode" in which the beam is localized in a single area. The surfcae morphology of flyash particles were determined using SEM. For physical properties, Indian (IS) and (ASTM) Standard Test Methods were used. Figure 2 shows the picture of flyash and common soil sample used in the study.

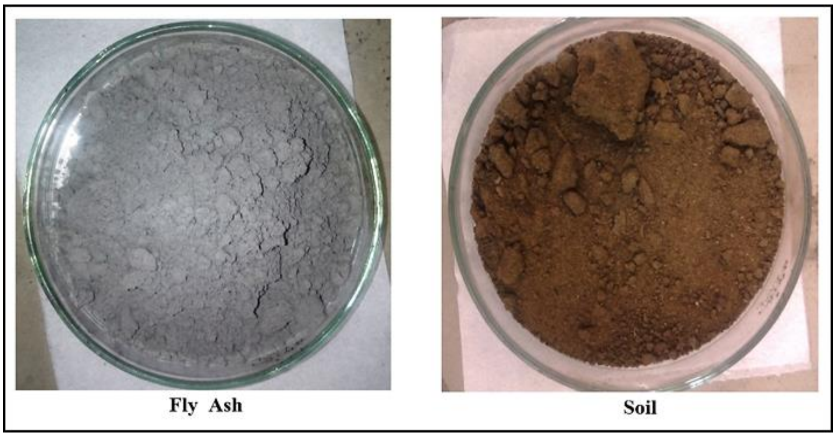


Figure 2. Typical Class F flyash and Soil Colour

3. Results and Discussion

3.1. Chemical Analysis of Class F Flyash

Class F flyash sample collected from the site and the common soil sample has been subjected to study herein. The physicochemical characteristics of Class F flyash are significant features for deciding economic utilization of flyash. It is relevant from the calculation that the percentage of CaO was found to be 1.31% in the given sample classifying it to be Class F flyash category defined by [2]. The compounds SiO_2 and Al_2O_3 are major constituents of flyash which were measured at their highest concentration i.e. 35.23% and 22.59% respectively. The constituents in flyash under study showed vast variations in their chemical composition due to the quality of Indian coal and lack of standardization in the plant machinery. The descending order of fixed carbon is pursued with increase in densities of the fractions which is due to higher percentage of mineral content of the fractions with smaller particle size.

The flyash pH value influence the time of setting of geopolymer paste [18], pH test was done by dissolving flyash into distilled water and then pH measurement was done after 24 h. Here in this study, pH value observed for flyash sample was 7.30 whereas pH value of the soil sample used as standard was 7.80. As per the literature review, flyash pH value ranges from 8 to 11 and it tends towards rapid setting. pH value of flyash has close correlation with its CaO content. High CaO content in flyash resulted in higher pH value [18]. Further, the sample of flyash was subjected to FTIR to study the presence of functional groups in the sample as shown in Figure 3. For the chemical characterization of flyash, FTIR technique is applied. FTIR data indicates the presence of functional groups on the surface of flyash samples. FTIR analysis represents band at 1041 cm^{-1} showing Si-O-Si and Si-O structure. The band is observed at 795 cm^{-1} representing Si-O structure, Si-O-Al structure (Al, Mg)-O-H Al-O-(Mg, Al) structure [19].

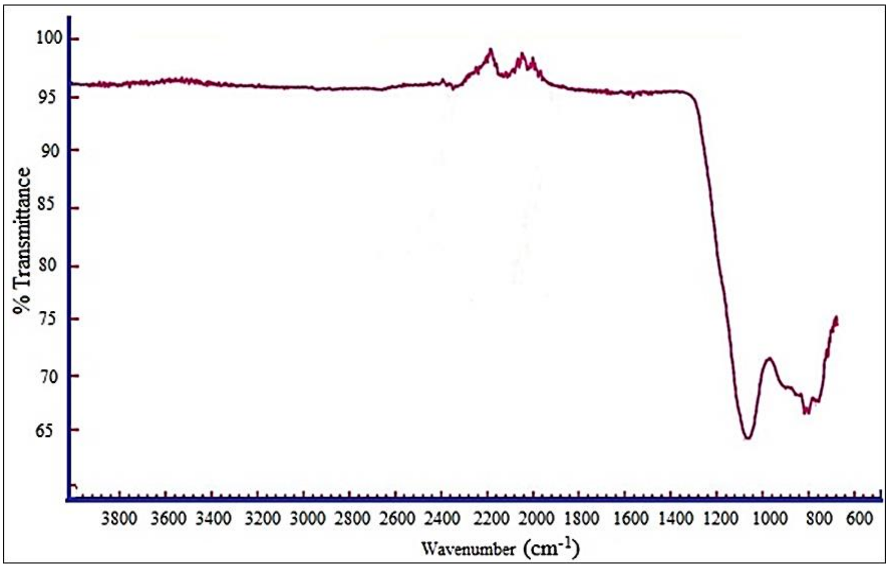


Figure 3. FTIR of Class F flyash sample

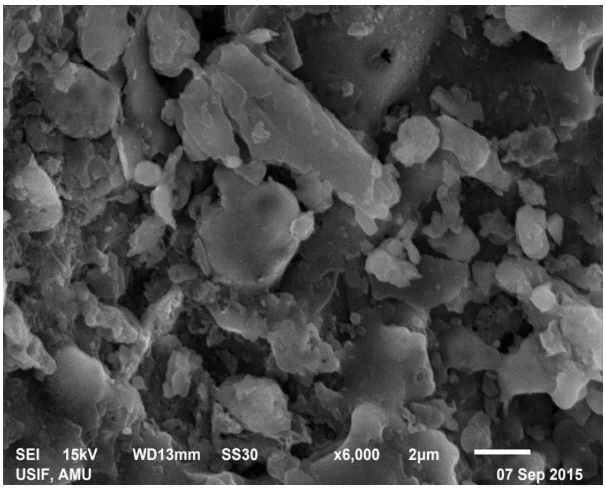
The flyash samples were also examined for their chemical composition. The identified elements in the ash sample were found to be C, O, Al, Si, K, Ca and Ti in various compound forms (Al_2O_3, SiO_2, K_2O, CaO, TiO_2 etc.). The quantitative result from point analysis of Class F flyash used in the study is shown in Table 2. The chemical composition may be cross verified by SEM-EDS technique as well that provide detailed information regarding morphology and surface texture of individual particles with elemental composition of samples. SEM is most widely used for the chemical characterization of ash.

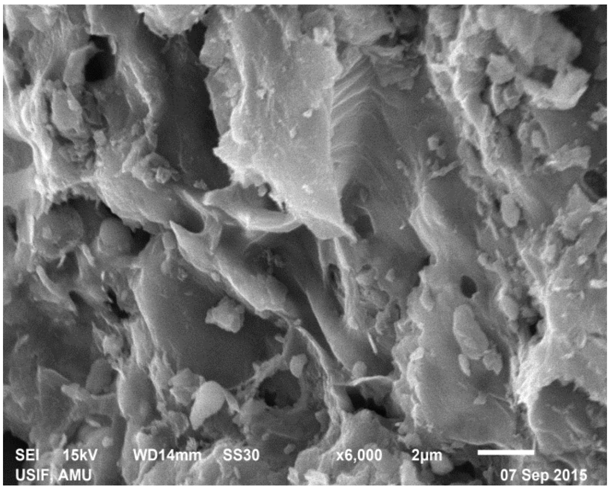
Table 2. List of elements with their weight (%) and atomic (%) present in Class F flyash

Element	Weight %	Atomic%
C	14.42	21.05
O	54.59	59.83
Al	11.96	7.77
Si	16.47	10.29
K	0.73	0.33
Ca	0.94	0.41
Ti	0.88	0.32

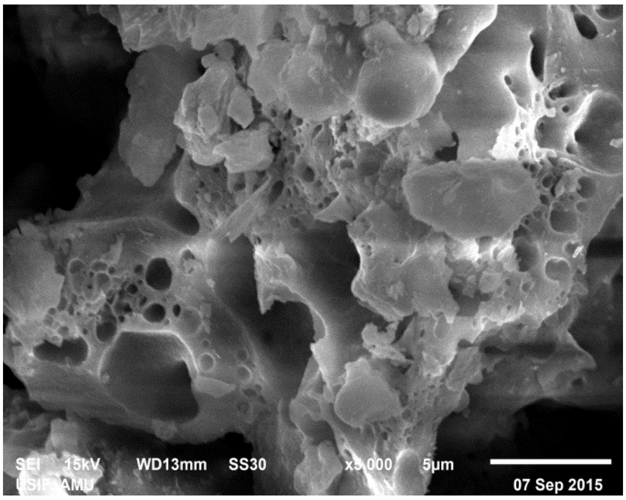
3.2. SEM/EDS Analysis

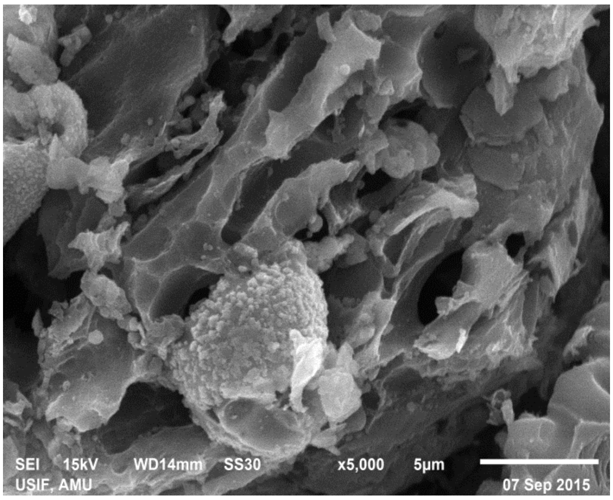
The surface morphology characterization has a critical role in understanding the chemical and physical behavior of the material. SEM is a technique used to study different modes of association and detection of irregularities on surface. SEM is used in the study to investigate the surface morphology of the sample. Figure 4 shows SEM images recorded for sample Class F, flyash surface at x2000, x5000 and x6000 magnifications. Figure 4(a) and 4(b) shows the presence of irregular shaped particles of variable size, covered with relatively smooth grains of quartz. The micrographs in Figure 4(c) and 4(d) also designated dark areas as organic materials, light areas as mineral matter and gray as mixture of coal and ash. The solid and porous part indicated the presence of mineral matter most likely quartz, which is supported in earlier study [19]. The partially burnt coal particles were shown by irregular black porous parts. The particle size 10µm at WD 13mm appeared to be spherical with small bulging of siliceous and aluminous glass in Figure. 4(e). EDS study of flyash sample suggested the presence of Carbon, Oxygen, Aluminum, Silicon, Potassium, Calcium, and Titanium as the primary element. Thus, it is clear from the discussion given above that SEM/EDS is useful tool to study the morphology and surface texture of individual particles as well as elemental composition of samples. The identified elements in the flyash samples were found to be C, O, Al, Si, K, Ca and Ti, in various compounds (Al_2O_3, SiO_2, K_2O, CaO,TiO_2 etc.) as determined by EDS.



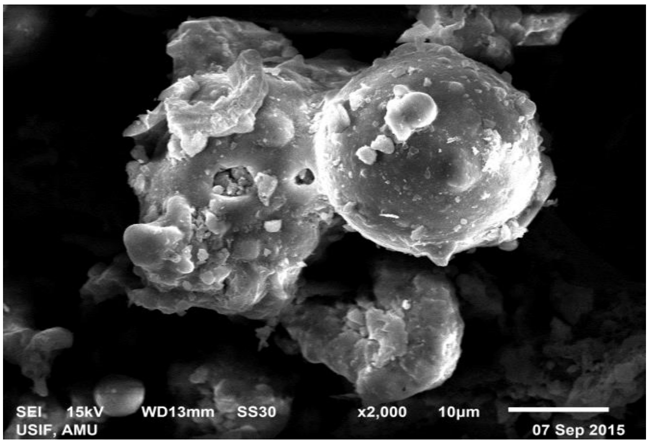


(a) SEM image of class F flyash sample (size: 2µm) at WD 13mm; (b) SEM image of class F flyash sample (size: 2µm) at WD 14mm





(c) SEM image of class F flyash sample (size: 5µm) at WD 13mm; (d) SEM image of class F flyash sample (size: 5µm) at WD 14mm



(e) SEM image of class F flyash sample (size: 10µm) at WD 13mm

Figure 4. SEM micrograph of Class F flyash with different particles size a) 2µm at WD 13 mm; b) 2µm at WD 14mm; c) 5µm at WD 13 mm; d) 5µm at WD 14 mm and e) 10µm at WD 13mm

3.3. Physical Analysis of Class F Flyash

The physical analysis is one of the most important parameter for selection and consideration of material in the civil engineering construction industry. Its geotechnical property makes it a good substitute of soil and the required percentage provide the general range of physical geotechnical properties available in the flyash sample. As determined in the present study, the physical properties of Class F flyash are listed in Table 3. The physical properties of locally available common Indian soil are selected for the comparison as provided in Table 3. The typical variations of comparative study obtained by Table 3 and plotted in Figure. 5. The sample of locally available common soil tested at 1.5m, 3.0m, 4.5m, 6.0m and 7.5m for comparison with Class F flyash sample is shown in Figure 5. It is found in the study that the physical properties of Class F flyash is very close to the relative values of common soil though it may differ from one country to another on their geographical conditions.

There are several reasons for the difference in soil regionally. The most significant factors include the parent soil, the climate and terrain of the region as well as the type of plant life and vegetation present and of course, human influence. In this study, the focus is on the geotechnical functions of the flyash and its comparison with the common soil which is an important criterion to replace any natural material. The strength and durability are two important factors to replace any material in the construction industry. A material is considered as a suitable building material if it possesses engineering properties suitable enough for construction works. These properties of building materials are responsible for its quality and capacity and help to decide their applications. A series of experiments conducted [20] had shown to improve the soil properties viz. texture, structure and bulk density. The permeability of clay loam soil increased from 0.54cm/hr to 2.14cm/hr by the addition of 50% flyash whereas it decreased from 23.80cm/hr to 9.67cm/hr in sandy soil by 50% fly-ash addition. The water holding capacity of sandy soil also increased from 0.38cm/cm to 0.53cm/cm at 50% level. Indian flyash is alkaline in nature; hence, its application for agricultural soil could increase the soil pH and thereby neutralize acidic soil [21].

Table 3. Summary of test results for different experiments on Class F flyash

Experimental Parameters	Class F Flyash	Common soil
Bulk Density (gm/cc)	1.25	1.3–1.7
Specific Gravity	2.12	2.5-2.8
Plasticity	Lower or non-plastic	Lower or non-plastic
Maximum Dry Density (gm/cc)	1.2875	1.3-2.4
Optimum Moisture Content (%)	18	5.0-30.0
Angle of Internal Friction(degrees)	28	30-40
Cohesion (kN/m^2)	2.1	Negligible
Permeability (m/sec)	1.650×10^{-5}	8×10^{-6} - 7×10^{-4}
Shrinkage Limit (Vol stability)	Higher	Low - high
Grain size	Major fine sand range / and very small percent of clay size particles	Major sand size fraction / silt and clay fraction and small percent of gravel size fraction
Clay (percent)	Negligible	Low- medium
Free Swell Index	Very low	Very low
Classification (Texture)	Sandy silt to silty loam	Sandy clay, silty clay, clay loam and silt loam
Water Holding Capacity (WHC) (percent)	40-60	10-70
Porosity (percent)	30-65	15-75

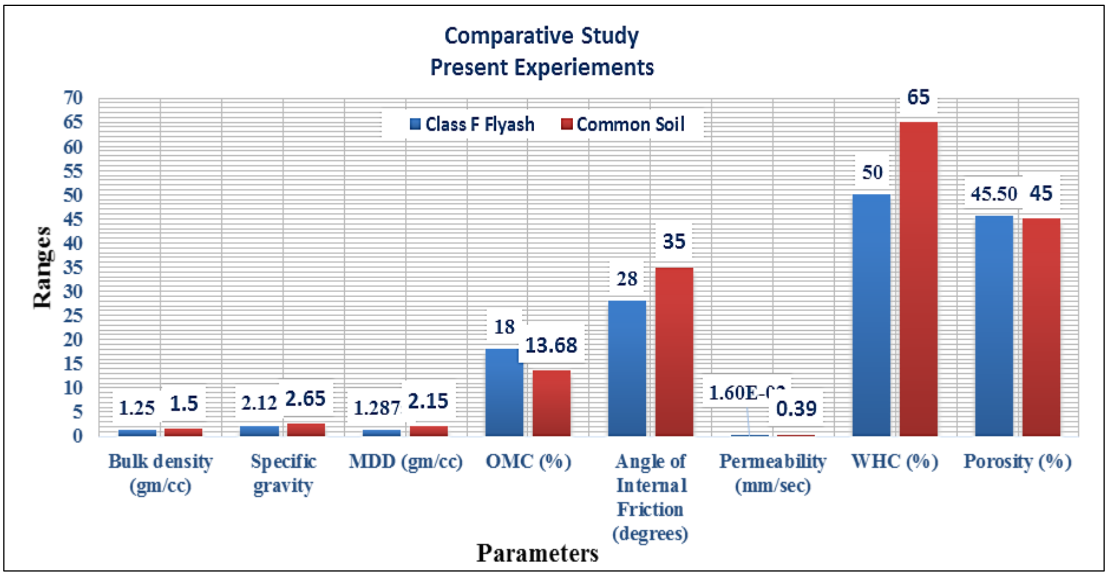


Figure 5. Comparative study of Class F sample and common soil sample

The specific gravity of flyash is 2.12 as determined by density bottle method. The sample of flyash and common soils were analyzed by using different sieve sizes. For consistency, the gradation of flyash was kept same as that of the common soils. The gradation of Class F sample and common soils were obtained by sieving as shown in Table 4. In the case of flyash sample, % finer was found to be 99% by hydrometer analysis. It was found that the diameter of the flyash particles ranges from 0.005 to 0.600 mm as shown in Figure 6. The locally available common soil sieve analysis results are plotted in Figure 7 that shows about 65% particles passing 0.075 mm fall in clay and silt range. By the above discussion, it has been figured out that the Class F flyash particles are coarser than common soil.

Table 4. Gradation of Class F flyash and common soil samples

Opening size (mm)	Class F Sample	Percent Passing (CS-1.5)	Percent Passing (CS-3)	Percent Passing (CS-4.5)	Percent Passing (CS-6)	Percent Passing (CS-7.5)
0.425	99.0	100	100	100	100	100
0.300	98.4	92.0	99.8	98.0	97.6	100
0.212	93.4	85.5	96.5	94.0	93.8	99.4
0.150	82.6	78.0	89.2	89.0	87.2	96.0
0.075	12.6	61.0	57.3	77.0	58.7	69.6

Optimum Moisture Content (OMC) and Maximum Dry Density (MDD) γ_d of the Class F flyash and common soil were determined by the Proctor's compaction test. The main aim of this test is to arrive at a standard which may serve as a guide and basis of comparison for the field compaction. Finally, a graph of moisture content vs dry density of Class F sample is plotted as shown in Figure 7. Locally available soil at 1.5m, 3.0m, 4.5m, 6.0m and 7.5m is shown in Figure 8. OMC is found to be 18% against γ_d 1.2875 g/cc for Class F sample which is close to the range of common soil found maximum at 6.0 m depth from the ground and 13.68 % against the γ_d 2.15 g/cc.

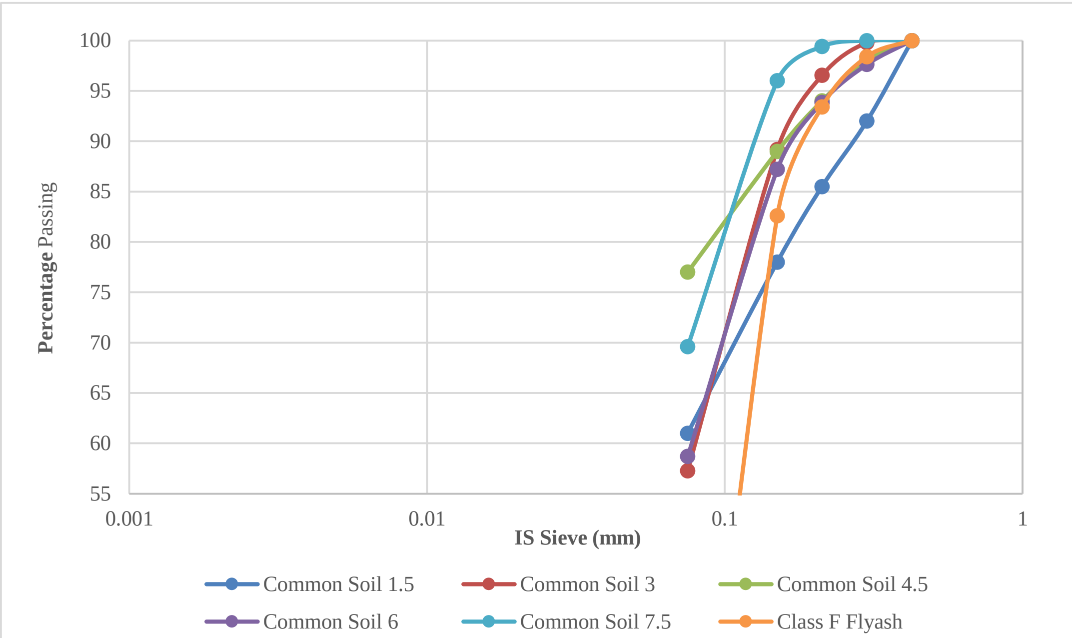


Figure 6. Particle size distribution characteristics for Class F flyash and soil sample

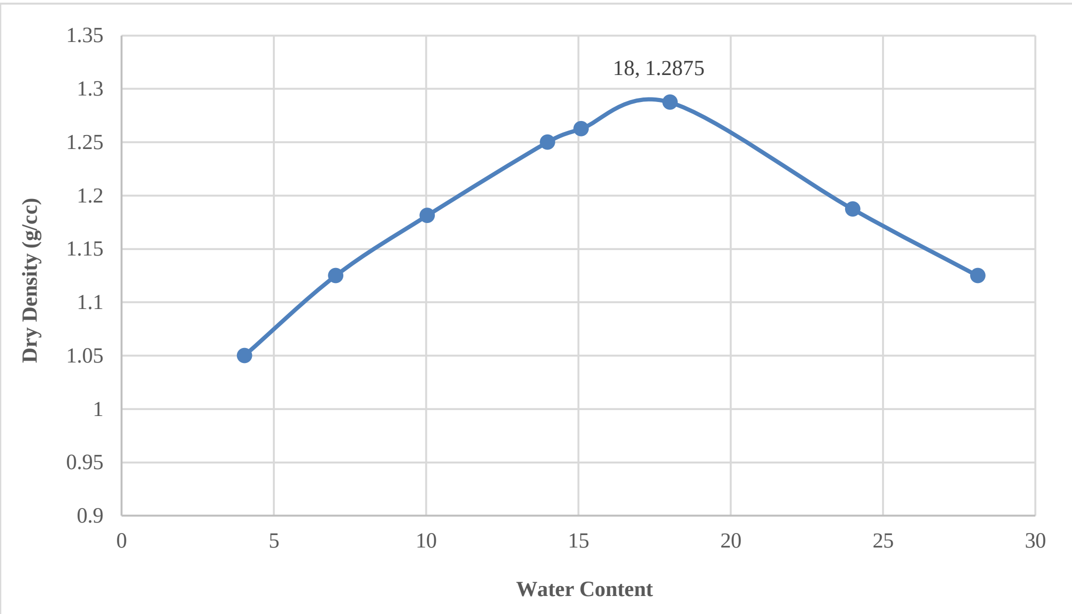


Figure 7. Variation of OMC and MDD of Class F sample

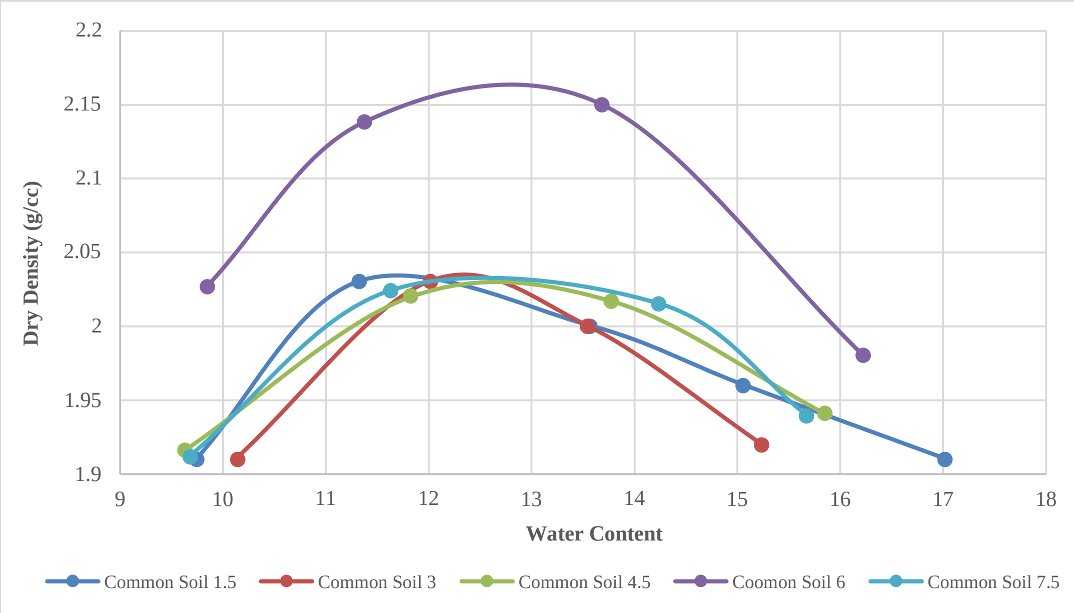


Figure 8. Variation of OMC and MDD for locally available soil sample at different depth

As seen in Table 3, the permeability of the Class F sample was found 1.650 × 10^{-5} m/sec. In general, the permeability of soil is measured using a permeameter test following either the constant-head or falling-head method. The former method is recommended for coarse-grained soils where k is expected to be smaller than 10^{-5} cm/sec, or when the soil contains 90% or more particles that are retained on 75µm sieve [22]. Conversely, the falling-head test is suited for testing fine-grained soils where k value is expected to be within the range of 10^{-5} to 10^{-8} cm/sec, or when the soil contains 10% or more particles passing 75µm sieve. Therefore, the falling-head method was selected in this study for testing Class F flyash sample containing fine particles such as silica.

4. Control Point of the Study

The tonnes of flyash produced every year because of the massive coal consumption have proved to be hindrance in developing optimized and cost effective techniques for reusability. The recycling of flyash will conserve the natural raw materials and reduce the disposal cost. It will also create new revenues and business opportunities while protecting the environment. Based on the experimental results, the following control point can be drawn:

- The identified elements in the flyash sample were found to be C, O, Al, Si, K, Ca and Ti in various compound forms (Al_2O_3, SiO_2, K_2O, CaO, TiO_2 etc.).
- The percentage of CaO was found to be 1.31% in the given sample classifying it to be Class F flyash category.
- pH value observed for flyash sample was 7.30 whereas pH value of the soil sample used as standard was 7.80. As per the literature review, flyash pH value ranges from 8 to 11 and it tends towards rapid setting.
- pH value of flyash has a close interconnection with its CaO content. Excessive CaO content in flyash upshot in higher pH value.
- FTIR analysis represents the band at 1041 cm^{-1} showing Si-O-Si and Si-O structure. The band is observed at 795 cm^{-1} representing Si-O structure, Si-O-Al structure.
- The specific gravity and bulk density of Class F samplewere found in the range of common soil sample i.e., is 2.12 and 1.25.
- The sample of flyash and common soils were analyzed by using different sieve sizes. The particles of Class F sample found coarser than a common sample.
- O.M.C is found to be 18% against MDD (γ_d) 1.2875 g/cc for Class F sample which is close to the range of common soil found maximum at 6.0 m depth from the ground and 13.68 % against the (γ_d) 2.15 g/cc.
- The porosity test results of Class F sample show higher initial value than common soil but variation is within the acceptable limit.
- The significance of moisture composition is very high in the permeability of fresh Class F sample. Such computation and evaluation can be utilized for stability analysis of earthen structures. The permeability results of the present study have been found in the perfect match with the range of common soil.

5. Conclusion

In India, the majority of flyash produced fall in Class F. ASTM C618 Class F flyash samples have been examined in the present study. This study shows the chemical and physical suitability of Class F flyash in the construction industry. Since flyash ties up free lime which leads to less bleed voids, it leads to a considerable reduction of permeability to water and sulfate as aggressive chemical. Moreover, in case of sulfate attacks the experimental results in published studies on Class F flyash shows that use of 20% flyash as replacement of Portland cement cause a slight difference in strength properties of the samples. It also reveals that all physical properties are much closer than available common soil. By using Class F flyash, the amount of soil used in the production of soil based construction materials i.e., bricks, roof tiles, and blocks etc. can be reduced. The economic benefit can be achieved by using flyash as a pozzolanic addition in the concrete mixture and mixed mortar. In conclusion, the use of additional waste materials provide both durable and economic building construction and ecological balance. For the Indian condition, it is recommended that Class F flyash can be used as a general fill in construction activities i.e., buildings, roads, embankment, and low lying areas. In contrast with generally used fill material (local soils) Class F flyash is a lightweight material. India is an agriculture-based country. The excessive and unsuitable usage of soil result in nutrient exhaustion, abrasion and other forms of losses, the soil productivity declines; it lessens the accessible areal domain for agricultural utility. By utilizing flyash as fill material, an equal volume of topsoil which will otherwise be used in filling can be saved.

6. Acknowledgement

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7. Conflicts of Interest

The authors declare no conflict of interest.

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