CHARACTERISATION OF FLY ASH FROM COAL-FIRED THERMAL POWER PLANTS USING ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY

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ABSTRACT

Fly ash composition is useful in predicting slagging and fouling characteristics of combusted materials as well as the potential utilization of ash by-products. The ash composition analysis can also be helpful in developing a pollution abatement approach for various applications of fly ash such as cement and ceramics manufacturing. The current study deals with the characterisation of fly ash samples collected from different NTPC units in India for eleven major oxides (Na_2O, MnO, SO_3, P_2O_5, MgO, K_2O, TiO_2, CaO, Fe_2O_3, Al_2O_3 and SiO_2) and eleven trace elements (As, Co, Pb, Ni, La, Cu, Zn, Cr, V, Sr and Ba) by non-destructive technique, ED-XRF. Procedure developed was validated using NIST certified coal ash reference materials. Among the major elements, the concentration of SiO_2 is found to be the highest in the range of 51.36-58.5% and that of Na_2O is found to be the lowest in the range of 0.02-0.17%. Among the trace analytes, Ba content is found to be the highest in the range of 126.6-1393.5 ppm and As is found to be the lowest concentration in the range of 24.8-37.4 ppm, respectively. The study reveals that all the fly ash samples were of siliceous type as per IS: 3812.

Key words: Major oxides, Trace elements, Elemental analysis, ED-XRF, Fly ash.

INTRODUCTION

Major source of Power Generation in India is coal, accounting for nearly 61% of total power generation. Coal combustion results into generation of huge amount of fly ash. The ash content in Indian coals varies between 10-40%. An increase of 1% in the ash content can result in an increase in coal consumption of 3-4% affecting calorific value and in turn quality of coal[1]. Presently, National Thermal Power Corporation (NTPC) generates around 59 million tonnes of coal ash annually from its coal based thermal power plants[2]. The generation of huge quantities of coal ash poses serious disposal and environmental problems.

The major composition of fly ash is qualitatively similar to that of natural earthy materials such as soils and shales. Oxides of Si, Al, Fe and Ca account for nearly 90% of the composition of fly ash. Other elements such as Mg, K, Na, Ti and S occur as minor constituents and account for < 1% of the bulk

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composition. Fly ash is associated with various useful constituents such as Ca, Mg, Mn, Fe, Cu, Zn, B, S and P along with appreciable amounts of toxic elements such as Cr, Pb, Hg, Ni, V, As and Ba[3]. The distribution of each element within the fly ash structure is different, however; the smaller the particle size, the higher is the trace elements content due to the increase in the surface/weight ratio. The alkaline content depends on the concentration of the basic oxides (CaO & MgO) and the amount of acidic substances such as SO_2, SO_3, and P_2O_5 which are also present in the coal fly ash[4].

The physical properties of the coal fly ash, such as moisture content, particle mass, glass composition, and the portion of unburnt carbon, are dependent on coal properties, the combustion temperature of the coal, the air flow/fuel ratio, coal pulverization size, and the rate of combustion. The mineral constituents of the fired coal are responsible for the chemical composition of fly ash[5]. Only a detailed study of the physical, chemical and morphological properties of a particular fly ash could enable an understanding of the potential environmental and health impacts associated with its disposal and use; however, these have not been adequately investigated[6].

Coal ash has a great potential for utilization in producing building materials such as cement, concrete mix, bricks, pozzolana and waste water treatment besides its agronomic value as a soil conditioner and a source of soil major and micro-nutrients[7-10]. Fly ash is used in the construction industry as a substitute to aggregates and cement in concrete production. Basic fly ash (class F) is utilized in acid mine drainage mitigation[11]. It has also been used as an adsorbent for flue gas cleaning and as raw material in the synthesis of geo-polymers[12, 13]. Since the composition of fly ash vary depending upon source of coal, characterisation of fly ash from different thermal power stations throughout the country was felt necessary. The characterization of fly ash, it's potential for utilization and potential hazards to plants and animal were reviewed[14]. In view of the potential of fly ash as both a health hazard and useful raw material for recovery of radioactive and valuable elements, studies on elemental composition of fly ash are highly desirable.

In general, the method for elemental analysis involves using a solvent, dissolving the samples in nitric acid, and analysing the acid solution by spectroscopic means such as inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS) or graphite furnace atomic absorption spectrometry (GFAA). These procedures are time consuming and destructive in nature and can induce losses of some volatile elements (As, Pb, Se, Sb and Zn).

Multi-element analytical techniques like Neutron activation analysis (NAA), Particle-induced X-ray emission (PIXE) and Total reflection X-Ray fluorescence (TXRF) can be employed for the direct multi-element determination of major and trace elements in fly ash, but the use of NAA, PIXE[15] and TXRF[16] are limited as they are expensive and not widely available. Various techniques have been employed in the elemental analysis of fly ash, including X-ray fluorescence (XRF)[17-21].

Energy dispersive X-ray fluorescence (ED-XRF) is a multi-elemental and non-destructive technique applied for the analysis of geological, environmental, metallurgical, ceramic, and a wide range of other inorganic materials[22,23]. Advantage of this rapid technique is that it requires only little sample preparation. By measuring the intensity of the dispersed energies, it is possible to determine the constituted element(s) quantitatively.

EXPERIMENTAL

Materials and methods

The instrument used for this study consists ED-XRF spectrometer of model EX-6600SDD supplied by Xenemetrix, Israel. The spectrometer is fitted with a side window X-ray tube (370W) that has Rhodium

as anode. The power specifications of the tube are 3-60 kV; 10 µA- 5833 µA. Selection of filters, tube voltage, sample position and current are fully customizable. The detector SDD 25 mm^2 is having energy resolution of 136eV ± 5eV at 5.9 keV Mn X-ray and 10- sample turret enables keeping and analyzing 10 samples at a time. The quantitative analysis is carried out by the In-built software nEXT. All the samples and reference materials were analysed by the equipment mentioned above at NTPC-Energy Technology Research Alliance (NETRA), Greater Noida and IGCAR, Kalpakkam.

pH of the fly ash samples was carried out by electrometric method as given in IS: 2720 (Part 26)-1987. The Loss on ignition (LOI) values were obtained following ASTM standard C311 – 05, standard test methods for sampling and testing fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete.

Sample preparation

The particle size of the sample significantly influences results of XRF analysis for heterogeneous solid samples. Hence, it is of utmost importance to have strict control of the sample preparation procedure so that homogeneity of the sample is preserved. In the present study, fine grinding of the sample was carried out to reduce x-ray mineralogical and particle size effects and to improve sampling precision.

At NETRA, Greater Noida, fly ash samples were cleaned, crushed and sieved through 45 µ mesh[24] and were taken up for analysis in a plastic cup with prolene film base in the powder form. At IGCAR, Kalpakkam, a part of cleaned fly ash samples were taken for elemental analysis. Crushed and sieved (45 µ) samples were taken for oven drying for 4 hours at 80°C. After drying, the samples were placed immediately in a desiccator with fresh silica gel. Samples were weighed after allowing a minimum of 2 hrs to establish temperature equilibrium. Two gram of the fine ground sample and 0.5 g of the boric acid were mixed. The mixture was thoroughly ground and pressed to a pellet of 25 mm diameter by applying a pressure of 15 tons/sq.in using automated hydraulic press.

Calibration

In the present study, calibration for fly ash composition for major oxides has been arrived at using Secondary target (Ge) and optimising voltage and current as 35 kV and 2555 µA, respectively while measurement time taken as 100s. The Characteristic K x- rays of Germanium, 9.8 keV were used to excite the elements present in the standards. The standards used in the calibration are NIST SRM-2689, SRM-2690, SRM-2691, SRM-1633B, and SRM-1633c, which were obtained from National Institute of Standard & Technology (NIST). To examine the validity of the data, NIST fly ash reference materials mentioned above were analysed as sample to revalidate the equipment and the percentage of error obtained for NIST 2691 is given below in Table 1 and 2.

Table 1: ED-XRF analysis of certified reference material NIST 2691 at NETRA & IGCAR

Oxide (%)	NIST certified value (%)	Value obtained by NETRA	% Error	Value obtained by IGCAR	% Error
Na$_2$O	1.47	1.49	1.2	1.47	0.1
MgO	5.17	5.28	2.1	5.06	-2.1
Al$_2$O$_3$	18.54	18.56	0.1	17.55	-5.3
SiO$_2$	36	36.22	0.6	33.21	-7.8
P$_2$O$_5$	1.17	1.15	-1.3	1.27	8.4

Oxide (%)	NIST certified value (%)	Value obtained by NETRA	% Error	Value obtained by IGCAR	% Error
SO_3	2.07	2.09	0.9	2.07	-0.03
K_2O	0.41	0.41	-0.2	0.4	-1.1
CaO	25.82	25.09	-2.8	26.33	2.0
TiO_2	1.5	1.58	4.9	1.49	-0.6
MnO	0.04	0.03	6.7	0.03	-1.0
Fe_2O_3	6.32	6.6	4.5	6.08	-3.8

Table 2: ED-XRF analysis of certified reference material NIST 2691 at IGCAR

Element (ppm)	NIST - certified value (ppm)	Value obtained by IGCAR	% Error
V*	295.7	302.3	2.2
Cr	68	59.3	-12.7
Mn	200	198	-1.0
Co	26	26.2	1.0
Ni	53	54.6	3.0
Cu*	112.8	121.1	7.4
Zn	120	110.8	-7.6
As	30	34.8	16.1
Rb#	117.4	118.7	1.1
Sr	2700	2535.5	-6.1
Ba	5900	5932.2	0.5
La*	94	93.95	-0.1
Pb	29	29.7	2.2
U#	9.3	9.2	-0.5

*,#Values are obtained using standard reference material NIST -1633b and 1633c, respectively

Validation

The NETRA Lab participated in the National Council for Cement and Building Materials (NCCBM) proficiency test. The results were compared with proficiency test assigned values using Z scores and given below in Table 3. For every result a z-score[25] was calculated using the formula: $z = x – X/\sigma^*$ where 'x' denotes the average value of the analyte concentration in the test material obtained from the results submitted by the laboratory, X is the reference value of the analyte concentration in the test material and σ^* is the standard deviation. According to International Harmonised Protocol, the z-score for an element in the range $-2 \leq z \leq 2$ can be taken as satisfactory results. The results obtained are found to have good agreement with assigned values validating the method adopted by NETRA for analysing the coal ash samples.

Table 3: Results comparison with NCCBM proficiency test results for coal fly ash samples

Procedure	XRS-FP values	NCCBM PT test values	% Error	XRS-FP values	NCCBM PT test values	% Error	Robust Z score	
Sample ID	**PT sample-A**			**PT sample-B**			**Between**	**Within**
Oxide	**Lab**	**Median NCCBM**		**Lab**	**Median NCCBM**		**Zbi**	**Zwi**
MgO	0.82	0.73	-12.3	0.83	0.74	-12.7	0.29	-0.18
Al_2O_3	29.2	29.19	-0.1	29.21	29.27	0.2	-0.02	0.44
SiO_2	59.32	58.54	-1.3	59.34	58.46	-1.5	0.62	-0.77
SO_3	0.14	0.14	0.7	0.14	0.16	15.6	-0.06	2.16
CaO	1.06	1.455	26.9	1.06	1.54	31	-1.28	-9.14
Fe_2O_3	4.18	3.78	-10.5	4.14	3.72	-11.2	0.56	0.86

Evaluation of physical properties of fly ashes

The details of coal fly ash samples collected from different coal mines/fields region wise along with their pH and LOI values were provided in Table 4. During XRS-FP analysis, LOI indicated better results with normalization method as most of the loss in weight during LOI test was due to Non-XRF elements i.e., Volatile compounds such as H_2O^+, CO_2, F, Cl, S; including small amount of K, Na (if heated for too long). In the process some compounds like Fe_2O_3 and $CaCo_3$ are likely to be added [O_2 (oxidation, e.g. FeO to Fe_2O_3), later CO_2 (CaO to $CaCO_3$)].

Table 4: Data on coal ash samples from 9 mines region-wise with their pH & LOI values

Plant name	Plant N-1	Plant N-2	Plant N-3	Plant N-4	Plant E-1	Plant E-2	Plant W-1	Plant W-2	Plant S-1
Source mines	CCL, ECL	CCL, ECL	CCL, BCCL	NCL	BCL, CCL, MCL, NEC, ECL	MCL	SECL	NCL	SCCL, MCL
Region	NCR	NR	NR	NR	ER	ER	WR	WR	SR
pH	8.15	7.32	6.27	6.08	11.04	7.36	5.24	6.09	12.62
CaO + MgO (%)	1.86	1.03	1.22	0.94	3.3	1.3	0.58	0.92	3.96
LOI (%)	0.4	1.6	0.8	0.8	1.7	0.3	0.5	0.2	0.2
SO_3 (%)	0.32	0.29	0.23	0.03	0.24	0.05	0.06	0.12	0.27
Bulk density (g/cc)	0.98	0.79	0.85	1.08	1.08	1.16	0.87	0.88	1.13
Specific gravity	2.27	2.33	2.17	2.26	2.26	2.14	2.19	2.16	2.26

Central coalfields Limited (CCL), North Eastern Coalfields Limited (NEC), Northern Coalfields Limited (NCL), Mahanadi Coalfields Limited (MCL), Bharat Coking Coal Limited (BCCL), South Eastern Coalfields Limited (SECL), Eastern Coalfields Limited (ECL), Singareni Collieries Co. Ltd. (SCCL), National Capital Region (NCR), Northern Region (NR), Eastern Region (ER), Western Region (WR), Southern Region (SR).

Concrete containing siliceous fly ashes generally requires a higher dose of air-entraining admixtures to achieve a satisfactory air-void system. This is mainly due to the presence of unburnt carbon, which absorbs the admixtures. Consequently, higher doses of air-entraining admixtures are required as either fly ash content of the concrete increases or as carbon content of the fly ash increases. The carbon content of fly

ash is usually measured indirectly by determining its loss-on-ignition (LOI). In the present study, LOI values are found to be in the range of 0.2-1.7%. The sulfate content of fly ash ranges from 0.08 to 0.2%. IS 3812 limits the sulfate content of fly ash to 3% when the material is to be used in concrete. Higher content of SO_3 in fly ash may cause deleterious expansion. pH of the fly ash is directly related to the availability of macro and micro nutrients. In India, fly ashes are generally have highly alkaline due to low sulfur content of the coal and presence of the hydroxides and carbonates of calcium and magnesium[26]. A significant correlation is found between pH and magnesium/calcium oxides as shown in the Fig. 1. The correlation coefficient (r) shows a strong positive relationship (0.98) and the coefficient of determination ($R^2 = 0.96$) indicates that 96 % of the samples have correlated well. There are a few sources that produce fly ashes with much higher alkaline levels (up to 12.62). These fly ashes tend to be very reactive as the alkalis raise the pH of the pore solution when they are mixed in concrete and the high pH accelerates the dissolution of the glass in the fly ash. Particular attention should be made to the (alkali-silica) reactivity of the aggregates when high-alkaline fly ashes are used in concrete. In the present study, pH of the fly ash samples is found to be in the range of 5.24-12.62. The density and specific gravity of nine fly ashes was found distributed between 0.79 to 1.16 g/cc and 2.14 to 2.33, respectively. Having low bulk density, fly ash addition to soil reduces the bulk density of the soil.
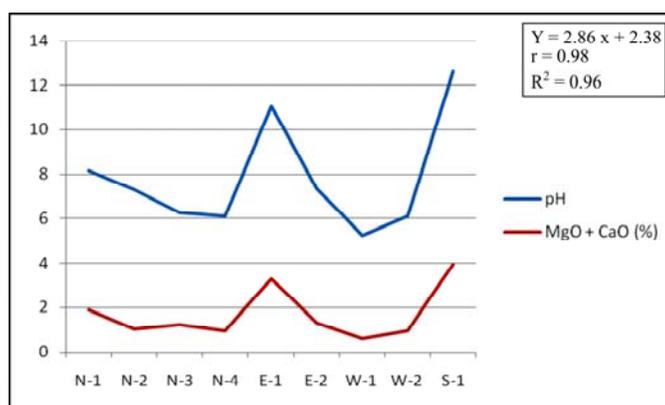
Fig. 1: Trend line for pH and total concentration of MgO & CaO

RESULTS AND DISCUSSION

Quantitative procedures employed in the present study are regression method at IGCAR and Fundamental Parameter Method at NETRA. Samples were analysed for metals such as Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn and Fe in duplicate. Results of IGCAR for major and trace elements (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3, V, Cr, Co, Ni, Cu, Zn, As, Sr, Ba, La and Pb) are given in Tables 5 & 5a. Results of NETRA for major elements are given in Table 5b. A typical spectrum of fly ash sample is depicted in Fig. 2 for major and trace elements.

Table 5: Major oxides of coal ash samples analysed by IGCAR

Oxide	Unit	Plant N-1	Plant N-2	Plant N-3	Plant N-4	Plant E-1	Plant E-2	Plant W-1	Plant W-2	Plant S-1	Range
		NCR	NR	NR	NR	ER	ER	WR	WR	SR	
Na_2O	%	0.04	0.04	0.03	0.03	0.15	0.05	BDL	0.03	0.07	0.03-0.15
MgO	%	0.65 ± 0.04	0.45 ± 0.02	0.44 ± 0.03	0.44 ± 0.01	1.22 ± 0.07	0.44 ± 0.05	0.28 ± 0.03	0.42 ± 0.01	1.26 ± 0.12	0.28-1.26
Al_2O_3	%	27.25 ± 0.06	25.57 ± 0.09	27.25 ± 1.49	29.24 ± 2.94	26.45 ± 0.32	27.39 ± 1.12	30.89 ± 1.53	31.05 ± 1.44	28.44 ± 0.73	25.57-31.05

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Oxide	Unit	Plant N-1	Plant N-2	Plant N-3	Plant N-4	Plant E-1	Plant E-2	Plant W-1	Plant W-2	Plant S-1	Range
		NCR	NR	NR	NR	ER	ER	WR	WR	SR	
SiO_2	%	49.78 ± 0.22	44.28 ± 0.73	50.53 ± 1.36	43.9 ± 1.83	48.96 ± 1.16	49.33 ± 1.05	54.26 ± 0.5	45.92 ± 0.55	55.73 ± 1.13	43.90-55.73
P_2O_5	%	0.53 ± 0.01	0.41 ± 0.01	0.42 ± 0.01	0.2 ± 0.01	0.31 ± 0.01	0.51 ± 0.01	0.21 ± 0.01	BDL	BDL	0.20-0.53
SO_3	%	0.32 ± 0.031	0.29 ± 0.002	0.23 ± 0.002	0.03 ± 0.027	0.24 ± 0.002	0.05 ± 0.016	0.06 ± 0.001	0.12 ± 0.002	0.27 ± 0.003	0.03-0.32
K_2O	%	1.03 ± 0.29	0.9 ± 0.47	0.97 ± 0.03	0.68 ± 0.01	1.44 ± 0.04	0.98 ± 0.02	0.99 ± 0.05	0.74 ± 0.01	1.49 ± 0.06	0.68-1.49
CaO	%	1.21 ± 0.001	0.58 ± 0.002	0.78 ± 0.004	0.5 ± 0.01	2.08 ± 0.001	0.86 ± 0.03	0.30 ± 0.004	0.50 ± 0.03	2.70 ± 0.03	0.30-2.70
TiO_2	%	1.78 ± 0.04	1.79 ± 0.03	2.05 ± 0.02	1.62 ± 0.02	1.81 ± 0.02	1.69 ± 0.01	1.74 ± 0.07	1.51 ± 0.13	1.38 ± 0.05	1.38-2.05
MnO	%	0.05 ± 0.001	0.05 ± 0.001	0.04 ± 0.0003	0.08 ± 0.002	0.07 ± 0.003	0.03 ± 0.0005	0.04 ± 0.002	0.09 ± 0.001	0.05 ± 0.003	0.03-0.09
Fe_2O_3	%	5.24 ± 0.2	4.79 ± 0.15	4.76 ± 0.12	5.09 ± 0.24	6.27 ± 0.04	4.26 ± 0.1	4.75 ± 0.11	6.14 ± 0.22	5.3 ± 0.08	4.26-6.27

Table 5a: Trace elemental data of coal ash samples analysed by IGCAR

El.	Unit	Plant N-1	Plant N-2	Plant N-3	Plant N-4	Plant E-1	Plant E-2	Plant W-1	Plant W-2	Plant S-1	Range
		NCR	NR	NR	NR	ER	ER	WR	WR	SR	
V	ppm	288.4 ± 6.6	260.4 ± 15.7	311.3 ± 7.4	275.2 ± 1.9	268.1 ± 4.2	272.8 ± 1.6	280.0 ± 17.6	245.2 ± 2.5	223.9 ± 3.7	223.9-311.3
Cr	ppm	110.9 ± 5.4	126.2 ± 2.0	140.8 ± 7.0	118.5 ± 1.1	126.6 ± 11.0	121.7 ± 12.0	121.2 ± 4.1	158.8 ± 4.2	114.8 ± 1.2	110.9-158.8
Co	ppm	33.5 ± 3.2	32.2 ± 5.1	32.7 ± 0.3	29.4 ± 0.2	38.2 ± 0.5	32.8 ± 0.2	33.0 ± 0.5	30.1 ± 0.1	38.7 ± 0.7	29.4-38.7
Ni	ppm	54.8 ± 1.9	72.6 ± 0.5	45.3 ± 0.8	60.5 ± 10.1	82.6 ± 2.1	53.2 ± 0.6	49.4 ± 5.6	68.9 ± 2.1	68.2 ± 1.7	45.3-82.6
Cu	ppm	98.5 ± 1.9	94.4 ± 4.0	95.4 ± 1.0	91.5 ± 0.8	92.4 ± 2.8	99.9 ± 1.5	88.7 ± 0.9	91.5 ± 3.4	90.2 ± 6.2	88.7-99.9
Zn	ppm	125.0 ± 4.4	126.5 ± 1.5	92.9 ± 2.2	122.8 ± 7.0	90.8 ± 4.1	128.1 ± 0.3	122.6 ± 6.5	128.1 ± 8.5	107.2 ± 1.7	90.8-128.1
As	ppm	36.3 ± 0.3	34.5 ± 1.9	31.5 ± 0.3	28.4 ± 0.5	24.8 ± 1.4	37.4 ± 1.1	33.1 ± 1.8	25.5 ± 2.0	26.4 ± 1.3	24.8-37.4
Rb	ppm	104.8 ± 4.2	111.6 ± 2.5	93.1 ± 0.2	68.7 ± 3.9	81.3 ± 0.2	91.0 ± 1.0	82.3 ± 0.3	72.5 ± 1.5	88.8 ± 0.5	68.7-111.6
Sr	ppm	375.5 ± 6.0	282.9 ± 5.9	280.4 ± 5.0	348.7 ± 4.7	524.1 ± 9.2	270.1 ± 3.0	251.8 ± 1.6	221.1 ± 3.9	506.8 ± 20.5	221.1-524.1

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El.	Unit	Plant N-1	Plant N-2	Plant N-3	Plant N-4	Plant E-1	Plant E-2	Plant W-1	Plant W-2	Plant S-1	Range
		NCR	NR	NR	NR	ER	ER	WR	WR	SR	
Ba	ppm	837.3 ± 67.0	795.2 ± 30.7	651.7 ± 111.8	1393.5 ± 30.0	914.8 ± 18.2	506.4 ± 20.5	126.6 ± 7.3	937.3 ± 62.7	770.1 ± 65.8	126.6-1393.5
La	ppm	90.1 ± 0.2	90.2 ± 1.0	92.1 ± 0.3	79.8 ± 0.7	88.6 ± 0.04	94.4 ± 0.5	101.5 ± 0.2	88.3 ± 0.02	91.4 ± 0.2	79.8-101.5
Pb	ppm	51.1 ± 1.1	49.1 ± 3.4	47.1 ± 1.2	38.0 ± 3.5	37.7 ± 0.5	54.5 ± 2.4	45.9 ± 2.2	33.7 ± 0.3	34.3 ± 0.5	33.7-54.5
U	ppm	9.0 ± 0.1	8.8 ± 0.01	9.1 ± 0.1	9.3 ± 0.2	9.3 ± 0.1	9.1 ± 0.1	9.4 ± 0.02	9.5 ± 0.02	9.1 ± 0.1	8.8-9.5

Table 5b: Major oxides of coal ash samples analysed by NETRA

Oxide (%)	Plant N-1	Plant N-2	Plant N-3	Plant N-4	Plant E-1	Plant E-2	Plant W-1	Plant W-2	Plant S-1	Range
	NCR	NR	NR	NR	ER	ER	WR	WR	SR	
Na_2O	0.01	BDL	0.01	0.02	0.19	0.02	0.02	0.05	0.17	0.01-0.19
MgO	0.98	0.84	0.79	0.76	1.11	0.79	0.65	0.69	1.16	0.65-1.16
Al_2O_3	28.74	29.02	29.4	28.18	24.14	28.37	28.32	26.44	24.92	24.14-29.4
SiO_2	58.5	58.43	59.52	61.47	60.67	60.83	62.03	62.9	61.27	58.43-62.9
P_2O_5	0.65	0.53	0.55	0.39	0.46	0.66	0.42	0.23	0.27	0.23-0.66
SO_3	0.09	0.1	0.1	0.09	0.11	0.08	0.09	0.08	0.2	0.08-0.2
K_2O	1.28	1.6	1.14	1.0	1.67	1.25	1.2	1.02	1.57	1.0-1.67
CaO	1.45	0.66	0.97	0.61	2.36	1.1	0.35	0.59	2.79	0.35-2.79
TiO_2	1.9	1.94	1.86	1.79	1.85	1.88	1.8	1.85	1.52	1.52-1.94
MnO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Fe_2O_3	5.28	4.94	4.64	4.65	5.53	3.97	4.07	5.6	4.35	3.97-5.6
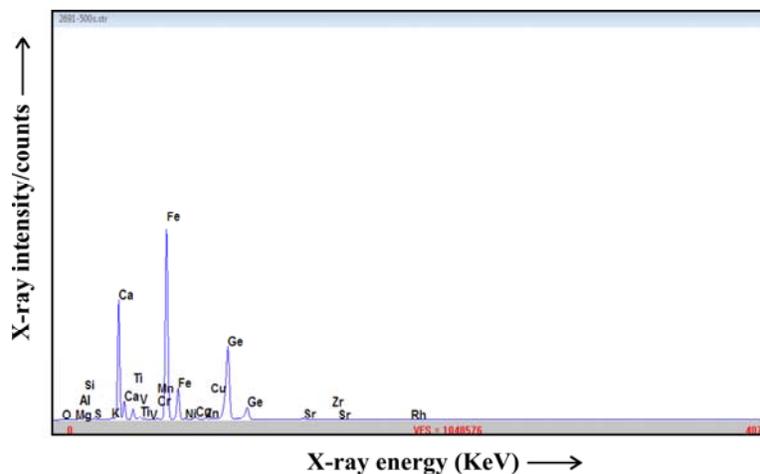
Fig. 2: Typical coal fly ash spectrum of ED-XRF for major and trace elements

The average results of ED-XRF analysis from both IGCAR and NETRA for the region wise fly ash composition from the nine mines were compared with IS: 3812 part-I Pulverized fuel ash specification and given in Table 6 below. The data on the results indicate that all the samples analysed were that of siliceous in nature. They are invariably produced from anthracite or bituminous coals and are predominantly composed by alumino-silicate glasses with varying amounts of crystalline quartz, mullite, hematite and magnetite. The high content of silica in all the samples qualify them credibility as good adsorbents[27]. There is a good agreement between IGCAR & NETRA results with respect to Silica, Alumina, Ferric oxide, Calcium oxide and magnesium oxide content. Among the major elements, SiO_2 is found to be the highest in the range of 51.36- 58.5 %, Na_2O is found having least concentration, in the range of 0.02- 0.17%. Among the trace analytes, Ba was found to be the highest in the range of 126.6- 1393.5 ppm and As was found at the lowest concentration in the range of 24.8-37.4 ppm, respectively. The value of potassium to rubidium ratio of the nine fly ash samples from different NTPC units in India was found to be in the range of 66.9-147.5, which is in good agreement with the average ratio of 128 for Indian coal fly ash reported[28].

Table 6: Comparison of the region-wise ash composition data of coal ash samples with IS: 3812

Stations/oxides (%)	Plant N-1	Plant N-2	Plant N-3	Plant N-4	Plant E-1	Plant E-2	Plant W-1	Plant W-2	Plant S-1	IS:3812	IS:3812
Region	NCR	NR	NR	NR	ER	ER	WR	WR	SR	**Siliceous**	**Calcareous**
CaO	1.33	0.62	0.88	0.56	2.22	0.98	0.32	0.55	2.75	Max. 10	Min. 10
SiO_2	54.14	51.36	55.03	52.69	54.82	55.08	58.15	54.41	58.5	Min. 35	Min. 25
$[SiO_2 + Al_2O_3 + Fe_2O_3]$	87.4	83.53	88.06	86.27	86.02	87.08	92.17	89.03	90.01	Min. 70	Min. 50
Na_2O	0.03	0.02	0.02	0.03	0.17	0.04	0.02	0.04	0.12	Max. 1.5	Max. 1.5
MgO	0.82	0.65	0.62	0.6	1.17	0.62	0.47	0.56	1.21	Max. 5.0	Max. 5.0
LOI	0.4	1.6	0.8	0.8	1.7	0.3	0.5	0.2	0.2	Max. 5.0	Max. 5.0
Type of fly ash as per IS 3812	**Siliceous**									**Siliceous**	**Calcareous**

CONCLUSION

The calibration procedure for characterising fly ash composition is developed for major oxides and trace elements. Measurement and the results are validated against the NIST certified reference material. It was found that ED-XRF can effectively be used for the analysis of fly ash samples. Results of the region-wise coal ash composition data of nine coal ash samples indicated siliceous type. Results of independent analysis by ED-XRF method at two different places gave good agreement. The trace elements in the ash can actually are beneficial to certain soils.

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