

Characterisation of coal and its combustion ash: recognition of environmental impact and remediation

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Abstract

Energy generation from coal poses an environmental drawback due to the abundance of some potential hazardous elements (PHEs). A few PHEs (As, Sb, Cu, Mn and Zn) are noticed in the coal collected from thermal power plants of India. Among them, As and Sb are depleted while Cu, Mn, and Zn are enriched in fly and bottom ash. The short- and long-term exposure of these PHEs into the ecosystem by emission, deposition, and leaching causes environmental contamination as well as pollution and health hazards. The water-leaching experiment shows that these elements have feeble mobilisation tendency and low risk. The bioavailability test reflects that bio-uptake of these PHEs into the human system may be the origin of several diseases. Proper storage and recycling of the large amount of fly and bottom ash is a serious concern of thermal power plants. Chemical characterisation of ash, including elemental mapping by scanning electron microscope, calculated enrichment ratio (ER), and relative enrichment index (REI) values, as well as lab-scale water-leaching experiments predict that combustion residues of the studied power generating unit are safe for utilisation in construction, geotechnical, and even in agricultural sectors. Chemical characterisation and pre-treatment of ashes before utilisation are urgently required to predict any possible contamination. Regular scrutiny of emission control device, proper management of ash disposal, and frequent utilisation are the keys for clean energy generation. A bottomless chemical and physical autopsy of coal by power plants prior to utilisation is the primary task for sustainable energy generation from environmental aspect.

1. Introduction

Coal has a significant share of the fuel used in global power production in a wide geographical range due to feasible economic cost and its reliable reserve (Verma et al., 2015; Saha et al., 2019). Major part of the world's electricity (nearly 37%) is generated from this fossil fuel (Bhangare et al., 2011; Saha et al., 2016; IEA Report, 2021). The presence of some potential hazardous elements (PHEs), e.g., Hg, As, Pb, Cu, and Zn, may contaminate or pollute the environment and damage the ecosystem (Finkelman, 2004; Dai et al., 2012). Combustion of coal in thermal power plants produces large amount of coal combustion residues (CCR) which are complex in nature (Vejahati et al., 2010). The subsequent removal, transport, and disposal of this large amount of heterogeneous waste are environmental problems for combustion power plants (Pandey et al., 2011; Verma et al., 2015). Emission, deposition, and leaching of these PHEs from ashes cause contamination of air, soil, sediment and water of the nearby dumping sites (Vejahati et al., 2010). The extended contamination of these PHEs may be a source of broad pollution and the bio-uptake of these hazardous elements may cause several diseases (Finkelman, 2004). Characterisation of coal and CCR is important for the recognition of the negative issue of coal combustion (Tang et al., 2013). The suitable disposal practice of ash and its reuse may be a solution to reduce the ecological pollution (Ahmaruzzaman, 2010). Studies on these two steps are urgently required to provide precise information to the coal combustion units for clean energy generation.

In India, generation of electricity is mainly depended on coal and large amounts of related residues are produced annually in thermal power plants. The purpose of this work is to characterise the feed coal, fly

ash and bottom ash collected from thermal power plant of eastern India with an emphasis of potential hazardous elements (PHEs). The study also aims to understand the environmental impact of these PHEs from combustion residues by leaching, emission, as well as bioaccumulation in the human system. This work also focuses on the possible suitable utilisation of these ashes in different environmental sectors and its pre-treatment before recycle. The management process of ash disposal is also discussed in this manuscript.

2. Material And Methods

2.1. Sampling

Gondwana coal and CCR (fly and bottom ash) were collected from four thermal power plants in West Bengal, an eastern state of India. The studied Plant 1 (Durgapur Project Limited), Plant 2(Durgapur Thermal Power Station), and Plant 3(Durgapur Steel Thermal Power Station) are situated in the Paschim Bardwan district and Plant 4 (Majia Thermal Power Station) is in the Bankura district of West Bengal. The installed capacities of plant 1, 2, 3, and 4 are 690 MW, 350 MW, 1000 MW, and 2340 MW, respectively. Raw feed coals were collected from feeders of each thermal power plant. Fly ashes were collected from electrostatic precipitator hoppers and collection of bottom ash samples were made from the output at the bottom of the boiler. All the sampling processes were conducted weekly during one month to obtain true gross sample. Samples were stored in PVC Zip-lock bag to avoid weathering and contamination. International organisation for standardization (ISO) recommendation was followed to obtain representative samples for laboratory experiment.

2.2. Methods

Analysis of proximate parameters (moisture, ash and volatile matter) of collected coal samples was done by Indian standard; IS: 1350, Part 1, 1984. Ultimate analysis (C, H, N, S) was done by CHNS Elementar analyser. Major oxides elements were analysed by ashing the coal samples at 850°C and 0.1 g of this ash was digested by a mixture of acid ($\text{HNO}_3 + \text{HCl} + \text{HF}$) in a ratio of 3:1:1 in a microwave oven (Tang et al., 2013; Saha et al., 2019). This digested solution was then run by inductively coupled plasma optical emission spectrometry (ICP-OES, model-VSTA MPX) to determine the concentration of major oxides in coal. The concentration of trace elements (Sb, Cu, Mn, Zn) in coal, fly ash, and bottom ash were find out by inductively coupled plasma mass spectrometry (ICP-MS, model-ELAN, DRC). To avoid polyatomic spectral interference As was determined by ICP-MS equipped with collision cell technology (Li et al., 2014). In this case, same digestion procedures were followed to digest the coal, fly ash, and bottom ash samples as mentioned above for major oxides elements analysis. All the instrumental examinations are carried out in triplicate and interference is avoided by measuring the spiked samples solution. Reference material SRM 1632d is used to check the quality control, quality assurance, and rationale of digestion procedure. All the analytical results were reported by air-dried coal basis. Volatile matter and fixed carbon were also calculated in dry ash free basis. Elements were also characterised by a Scanning electron microscope (SEM) equipped with dispersive X-ray spectrometry (EDS) in the representative combustion

ash sample. Minerals were determined by X-ray diffraction (model: Bruker, D-8 discover) in low-temperature ash (LTA, at 370°C) residues of coal samples. Scanning range of 10-70° 2 θ at a scan rate of 2°/min and Ni-filtered and Cu-K α radiation were used in XRD. In this case minerals, were identified by JCPDS software (ICDD, PDF 2 version 2009). In the water leaching experiment, about 10 g of each representative combustion residue (fly and bottom ash) was dissolved in 100 ml deionised water. This solution was left for a day and then agitated by a shaker (20 rpm) in a polypropylene centrifuge tube. The leachate was obtained by vacuum filtration and concentration was determined by ICP-MS. The bio-availability test of fly and bottom ash by HCl leachant was carried out by the method describe by Shim et al. (2005). Each fly and bottom ash sample (7.2 g) was taken in 240 ml of 1 (N) HCl maintaining the solid liquid ratio 3: 100. This solution was shaken by a laboratory shaker (20 rpm) in a polypropylene centrifuge tube. Finally, the solution was filtered by vacuum filtration and analysed by ICP-MS. All the leaching experiments were performed in triplicate for both fly and bottom ash from each thermal power plant to obtain a representative result. SPSS software was used for the statistical analysis in this study.

3. Result And Discussion

3.1. Coal Characteristics

The average proximate and ultimate parameters of coal samples collected from thermal power plants of West Bengal are represented in Table 1. The average ash yield of the collected coal samples vary within the range 31.26-37.52%. The moisture content of the coal of studied power plants is low (4.28-6.45%). The carbon percentages (C_{ad}) of collected feed coals are varies from 59.18 to 63.24% (Table 1). The examination of proximate and ultimate parameters shows that the coals of thermal power plants are in the range of high volatile bituminous to sub-bituminous rank (Taylor et al., 1998; Saha et al., 2019). The nearly equal values of proximate and ultimate parameters of feed coals of four different thermal power plants may be due to the supply of the fuel from mines of same geological origin (Bhangare et al., 2011; Saha and Roychoudhury, 2019).

Table 1
Proximate and ultimate parameters (%) of coal samples

	A_{ad}	VM_{ad}	FC_{ad}	M_{ad}	VM_{daf}	FC_{daf}	C_{ad}	S_{ad}	H_{ad}	N_{ad}
Plant 1	36.65	25.52	31.38	6.45	44.85	55.15	61.26	0.48	5.18	2.24
Plant 2	33.72	21.38	40.62	4.28	34.48	65.52	60.72	0.33	3.37	1.58
Plant 3	31.26	22.74	40.82	5.18	35.78	64.22	59.18	0.52	3.15	0.95
Plant 4	37.52	23.68	32.97	5.83	41.8	58.2	63.24	0.61	4.42	1.08

A, Ash; VM, Volatile matter; FC, Fixed carbon; C, Carbon; S, Sulfur; H, Hydrogen; N, Nitrogen; ad, Air dried basis, daf, Dry ash free basis

Mineralogical analysis by XRD reveals that quartz, kaolinite, illite, dolomite, apatite, calcite, siderite, pyrite, rutile minerals are present in the studied coal samples. This focuses that coal are enriched with various minerals and have notable influence of silicate, clay, sulphide, carbonate, phosphate, and oxide minerals (Ward, 2002; Saha et al., 2016). Minerals are the host of major and trace elements in coals which reflect the chemical quality of fuel utilised in thermal power plants (Dai et al., 2013). The phase transformation of minerals during combustion controls the fate and distribution of the associated elements into coal combustion residues (Vassilev et al., 2010; Hu et al., 2018).

The average concentration of major elements oxides of coal samples are depicted in Table 2. The analysis of coal ashed samples (850°C) by ICP-OES shows that SiO₂ has the highest concentration, followed by Al₂O₃. Fe₂O₃ has also notable concentration (7.22-11.56%) in the feed coal of all the studied thermal power plants. However, all other analysed major oxide elements (TiO₂, P₂O₅, MgO, CaO, Na₂O, K₂O, SO₃) concentration are low in range (Table 2). This result highlights that ash forming elements as well as alumino-silicate minerals had a dominant influence in the studied coal content (Dai et al., 2012; Saha et al., 2016).

Table 2
Average concentration (% air dried basis) of major elements oxides of coal samples

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	MgO	CaO	Na ₂ O	K ₂ O	SO ₃	LOI
Plant 1	48.27	32.12	7.44	1.18	1.86	1.93	1.72	1.88	1.66	0.48	1.46
Plant 2	56.15	25.43	7.22	1.06	1.18	1.68	1.75	1.64	1.55	0.42	1.92
Plant 3	54.34	21.07	11.56	2.88	1.76	1.58	1.02	1.05	1.96	0.96	1.82
Plant 4	58.28	21.26	8.85	1.94	1.98	1.77	1.52	1.94	1.05	0.38	1.03
LOI, Loss of ignition											

A few potential hazardous elements (PHEs) As, Sb, Cu, Mn, and Zn elements were analyzed in the collected coal samples. The mean concentration of these PHEs elements have low values (Figure 1) and most of these elements are within the world average concentration reported by Ketris and Yudovich (2009), except for Sb with a slightly higher concentration in the feed coals from studied thermal power plants compare to the world average (Figure 1). Several PHEs are reported by the researchers in coal of different geological age and geographical region (Finkelman, 2004; Saha et al., 2018). During combustion, these elements may undergo different chemical and physical transformations depending on the combustion temperature and technology applied in the thermal power plants (Hower et al., 1996; Saha et al., 2019). The distribution of these elements in significant amounts into the different segments of nature may cause environmental pollution and health hazards (Rowe et al., 2002; Saha and Roychoudhury, 2019). Therefore, examination of these PHEs in feed coal is important for the consumption in thermal power plants from environmental aspects (Markwiese et al., 2014). Because the range of concentration of the PHEs in the coal samples is at a considerable level, a regular chemical

analysis is urgently required for the burning of this fossil fuel in the thermal power plants because vulnerable exposure of the elements due to combustion may cause adverse effects on the environment (Finkelman, 2004; Saha and Roychoudhury, 2019).

The association of PHEs elements with major oxide elements are studied by R-mode hierarchical cluster analysis (Figure 2). The dendrogram was determined by using Euclidean distance and centroid clustering method (Eskanazy et al., 2010). The results show that Mn, Zn, and Cu are strongly associated with SiO_2 , Al_2O_3 , and Fe_2O_3 (Figure 2). The significant binding of these three elements with major ash-forming elements highlights their quartz, clay (e.g., kaolinite, illite) and pyrite occurrence in the coal samples (Finkelman, 1994; Dai et al., 2013). It is observed that the other two elements, As and Sb, show a completely different association with major oxides elements in coal (Figure 2). They have a significant association with Ca, Na, Mg, P, K, and Ti oxides. However, they show lack of association with SiO_2 , Al_2O_3 , and Fe_2O_3 . The reason may be due to least affinity of these elements towards the ash forming elements as well as low existence of pyrite in the analysed coal samples. The statistical study shows that As and Sb may have occurrence with carbonate (calcite, dolomite), phosphate (apatite), and oxide (rutile) minerals (Ward, 2002; Vassilev et al., 2010) which has been noticed in the XRD study of analysed coal samples. The knowledge of affinity of trace elements is important to understand the coal quality for utilisation because it determines the final residence of trace elements in the residues after burning of coal (Bhangare et al., 2011; Tang et al., 2013). Chemical and mineralogical information help to predict possible combustion and post combustion consequence due to emission, deposition, leaching and weathering of combustion residues (Dai et al., 2013; Verma et al., 2015).

3.2. Distribution and fate of PHEs elements in coal combustion ash

PHEs in coal are distributed in major combustion residues (fly and bottom ash) along with flue gas during combustion (Tiwari et al., 2014; Hu et al., 2018). The fate and distribution of these elements primarily depends on mode of occurrence of these elements in coal and mineral phase transformation at different temperature of combustion (Verma et al., 2015; Saha et al., 2018). In addition, physical and chemical technology applied in the thermal power plants also influences the distribution of PHEs in combustion residues (Li et al., 2012). The observed concentration of As, Sb, Cu, Mn, and Zn in fly and bottom ash are reported in the Table 3. The average concentrations of these elements in combustion residues of the studied thermal power plants are small in value ($\mu\text{g/g}$). However, Mn, Zn, and Cu have comparatively higher value than As and Sb in both fly and bottom ash. Vast coal combustion in thermal power plants throughout the India generates a huge amount of fly and bottom ash in every year (Bhangare et al., 2011; Verma et al., 2015). So, a cumulative content of these elements in the large amount of ashes generated in thermal power plants can cause environmental pollution (Zhou et al., 2013). Therefore, though the concentrations of the analysed elements are not in a significant range, a regular chemical analysis is required for environmental aspect (Tang et al., 2013; Saha and Roychoudhury, 2019).

Table 3
Concentration of PHEs ($\mu\text{g/g}$, air dried basis) in coal combustion ash

	Fly ash					Bottom ash				
	As	Sb	Cu	Mn	Zn	As	Sb	Cu	Mn	Zn
Plant 1	0.46	0.35	20.26	72.61	22.41	0.15	0.18	16.58	90.18	20.56
Plant 2	0.21	0.26	26.36	75.82	30.74	0.08	0.05	17.92	88.51	23.58
Plant 3	0.16	0.32	25.45	70.35	18.86	0.09	0.08	13.85	92.35	15.82
Plant 4	0.42	0.38	28.84	65.78	24.32	0.12	0.14	18.38	82.64	17.65

The chemical as well as physical transformation of coal at different temperatures during burning causes enrichment or depletion of the allied elements (Bhangare et al., 2011; Saha et al., 2019). A mathematical estimation of concentration of elements in combustion residues compare to coal was followed with reference to enrichment ratio (ER) and relative enrichment index (REI) to understand the fate of these elements after combustion (Vejahati et al., 2010; Tiwari et al., 2014). The values of ER and REI are calculated using the formula, $[\text{ER} = \text{element concentration in ash} / \text{element concentration in coal}]$ and $[\text{REI} = (\text{concentration of elements in ash} \times \text{ash percentage of coal}) / (\text{concentration of elements in coal} \times 100)]$, respectively. The result shows that Cu, Mn, and Zn are enriched in both fly and bottom ashes, however, As and Sb are depleted in both combustion residues (Table 4). This observation highlights that Cu, Mn, and Zn have affinity towards ash whereas, As and Sb have an tendency to be emitted with the flue gas (Hu et al., 2018; Saha et al., 2019). The relative high volatility of chalcophile elements As and Sb than rest of the three elements (Cu, Mn, Zn) is the cause for the spike in emission fraction with the vapour phase (Hower et al., 1996; Saha et al., 2019). Combined observation of cluster analysis along with calculated ER and REI values shows that Cu, Mn, and Zn have alumino-silicate occurrence (Figure 4) and are greatly captured into the ash (Table 4) (Vassilev et al., 2010; Verma et al., 2015). Alternatively, elements (As and Sb) which are not significantly associated with alumino-silicate minerals in coal or may loosely bind on surface of the Al-Si glass in the ash have a strong emission tendency (Vejahati et al., 2010). It is also observed that the ER and REI value of Cu and Zn are relatively high in fly ash compared to bottom ash. This may be due to the higher capturing capacity of small particle size and greater surface to volume ratio of fly ash than coarse bottom ash (Tang et al., 2013; Saha et al., 2019). Among the analysed elements, only Mn is slightly more enriched in bottom ash than fly ash because of the relative low volatility of Mn (Pandey et al., 2015; Hu et al., 2018).

Table 4
Enrichment ratio (ER) and Relative enrichment Index (REI) values of PHEs in ash

	Fly ash					Bottom ash				
ER values	As	Sb	Cu	Mn	Zn	As	Sb	Cu	Mn	Zn
Plant 1	0.21	0.15	2.4	2.37	1.23	0.07	0.08	1.96	2.94	1.13
Plant 2	0.31	0.3	1.63	1.78	1.1	0.12	0.06	1.11	2.08	0.84
Plant 3	0.35	0.3	3.16	2.17	1.61	0.2	0.08	1.72	2.85	1.35
Plant 4	0.26	0.12	2.78	2.31	1.06	0.07	0.04	1.77	2.9	0.77
REI values										
Plant 1	0.08	0.05	0.88	0.87	0.45	0.03	0.03	0.72	1.08	0.41
Plant 2	0.1	0.1	0.55	0.6	0.37	0.04	0.02	0.37	0.7	0.28
Plant 3	0.11	0.09	0.99	0.68	0.5	0.06	0.02	0.54	0.89	0.42
Plant 4	0.1	0.04	1.04	0.87	0.4	0.03	0.02	0.67	1.09	0.29
ER= element concentration in ash/ element concentration in coal										
REI= (concentration of elements in ash × ash percentage of coal)/ (concentration of elements in coal × 100)										

The ER and REI value of the PHEs of the studied thermal power plant are not in elevated range (Table 4) but protective measures are required to follow the clean energy generation protocol (Zhou et al., 2013; Saha et al., 2019). Because of the adequate and prolonged emission as well as leaching of these elements into the environment may cause pollution and health hazardous (Finkelman, 2004; Zhou et al., 2013). Regular monitoring of emission control device and modification of the emission control technologies are required to control atmospheric pollution from thermal power plants. Chemical characterisation of fly and bottom ash as well as suitable and frequent recycling is needed to combat against leaching of PHEs into the lithosphere and hydrosphere (Bhattacharyya et al., 2009; Markwiese et al., 2014).

3.3. Laboratory experiment for evaluation of environmental impact of combustion ash

Temporary storage and frequent recycling of huge amount of fly and bottom ash is a big issue for Indian thermal power plants (Verma et al., 2015; Saha et al., 2019). Generally, deposition of ash in ash pond is followed by the power plants and then this large amount of wetted combustion residues is primarily stored in the ground (Ahmaruzzaman, 2010). Mobility of these PHEs from coal combustion residues to hydrosphere and lithosphere from the nearby stockpiles of ashes may cause environmental contamination as well as further pollution due to prolonged exposure (Markwiese et al., 2014; Verma et

al., 2015). The extent of mobilisation of the trace elements depends on concentration of these elements in ashes, mode of occurrence, P_H of ashes, redox condition, and sorption or desorption reactions (Izquierdo and Querol, 2012; Saha et al., 2019). There have been various leaching procedures followed by the studies with different reagents and experimental conditions to understand the mobility of trace elements from ashes (Bhattacharyya et al. 2009; Izquierdo and Querol, 2012). In this study, leaching test with deionised water was conducted to understand the leach-ability of trace elements where original acidity or alkalinity of ashes i.e., P_H of combustion residues remains unchanged (Tang et al., 2013; Saha et al., 2019).

The result shows that water leachate concentration of all the analysed samples from both fly and bottom ash are in parts per billion (ppb, $\mu\text{g}/\text{kg}$) range (Figure 3). Among them, As and Sb have very feeble natural gradients in water. This may be due to their low concentration in ashes (Figure 1) and strong association with the ash matrix (Izquierdo and Querol, 2012; Saha et al., 2019). The presence of As as sparingly soluble arsenate species or retention as secondary species delaying the solubility are the reason of insignificant migration of As in water (Izquierdo and Querol, 2012; Zhao et al., 2018). Antimony is generally insoluble in all type of leachant; only few non-silicate fractions of Sb are the cause for poor extraction from ashes (Izquierdo and Querol, 2012), which also justify the experimental observation of this study (Figure 3, 4). Manganese and Zn have notable water leachate fraction in both combustion residues (Figure 3). This may be due to high concentration and surface association of these elements in ashes regardless their mode of occurrence (Tang et al., 2013). Amphoteric Zn metal generally shows increased mobility towards neutral P_H and Mn in glass is responsible for high solubility because of its light association (Li et al., 2012; Tang et al., 2013). Figure 3 shows that Cu has comparable high concentration in fly ash than bottom ash because of easy mobilisation from finer particles than coarse fraction (Izquierdo and Querol, 2012).

Deposition and leaching of the emitted particulate matter of toxic elements in the different environmental segments such as ground and surface water, soil, and sediment causes bioaccumulation and biomagnifications in the ecological pyramid (Bhattacharyya et al. 2009; Markwiese et al., 2014). This leads adverse effect into the food-chain and finally human health (Finkelman, 2004; Markwiese et al., 2014). A lab-scale bio-availability test is performed to measure the potential mobility of hazardous elements into the living system. The acidic medium of this lab-scale test is analogous with the P_H range of digestion process in stomach (Shim et al., 2004).

Figure 4 demonstrates the HCl leachant concentrations of trace elements from fly and bottom ash. The range of concentration of the leachates of PHEs is also in ppb range. However, this array of concentration ($\mu\text{g}/\text{kg}$) is a serious concern with respect to human health risk (Zhou et al., 2013). Arsenic and Sb show comparatively lower mobility in the acidic medium than in water (Figure 3&4). They show very minor concentrations for fly ash and are below the detection limit for most of the bottom ash samples (Figure 4). The small release of these two elements reflects their scarce bio-availability as well as low risk (Shim et al., 2004; Izquierdo and Querol, 2012). It is pertinent to mention that the remaining three analysed elements, Cu, Mn, and Zn, show higher release into the HCl medium. This draws attention towards their

bio-available tendency into the human body because Cu, Mn, and Zn have common enhanced gradient of mobility in acidic medium (Zhou et al., 2013). The high release of these elements from fly ash compared to bottom ash is due to their greater reaction in fly ash which has a large surface to volume ratio (Saha et al., 2019). The surface association in fly ash and, on the other hand, their matrix occurrence in bottom ash of these elements is an additional reason of the difference in leaching tendency (Tang et al., 2013). This bio-availability study reflects that uptake of these hazardous elements from combustion ashes in living system should be restricted to avoid health risk (Finkelman et al., 2002).

The both water leaching experiment and bio-availability test forecasts that prolonged and unrestrained mobilisation of the PHEs in the ecological segment can cause pollution as well as diseases (Finkelman et al., 2002; Saha and Roychoudhury, 2019). The leaching of these hazardous elements into surface water, ground water, soil, sediment, and air as well as bioaccumulation of these elements in the ecosystem creates a threat to the society (Izquierdo and Querol, 2012; Zhou et al., 2013). The direct exposure through emission and uptake of As with water and food can cause mild and severe problem in human like hypertension, hyperkeratosis even carcinoma depending on the degree of poisoning (Finkelman et al., 2002; Finkelman, 2004). The effect of large exposure of Mn and Zn creates neurological diseases (Finkelman, 2004; Saha et al., 2019). The availability of these metals leads to severe and widespread health problem in the local and also in the wider regions around the point source (Wilson and Robinson 2000; Markwiese et al., 2014).

3.4. Recycling of coal combustion ash

Disposal, management, and utilisation of huge amount of combustion bi-products are another major concern of thermal power plants from clean energy generation aspects (Yao et al., 2015). Coal combustion residue is considered as recyclable waste as well as important raw material for various applications (Ahmaruzzaman, 2010). These residues are commonly used in construction materials (cement, tiles, brick, ceramics, etc.), geotechnical sector (road, pavement, mine filling, reclamation of low-lying areas), and even in agricultural field throughout the world (Saha et al., 2019). The studied ash samples contain several major elements like Si, Al, Fe, P, Mg, Ca, Ti, and K (Figure 5) and PHEs (Figure 1). The ferro-alumino-silicate compositions of ashes along with some trace elements are also reported in the literature by the researches from different countries (Blissett and Rowson, 2012). Presence of these macronutrients (e.g. Ca, Mg, P, etc.) and micronutrients (Fe, Cu, Mn, Zn, Co, etc.) in the ash is essential for plants and animals in varying amounts (Ahmaruzzaman, 2010; Blissett and Rowson, 2012). However, existence of some toxic elements cause adverse effect in the environment due to recycling of this combustion waste (Bhattacharyya et al. 2009; Tang et al., 2013). Chemical characterisation of ashes is mandatory before utilisation in various sectors (Rowe et al., 2002). Nowadays, fly ash in agronomy has been potentially utilised because it helps to sustain soil quality by improving water absorbance capacity, bulk density, soil fertility, and P_H of soil (Basu et al., 2009; Blissett and Rowson, 2012). Additionally, the presence of essential macro and micro nutrients in ashes also aids to increase the agricultural yield and crop quality (Blissett and Rowson, 2012). The chemical characteristic of the analysed ashes shows that these ashes can be utilised in the agricultural field to improve the efficacy of irrigation land and products

(Basu et al., 2009). However, ash utilisation in agriculture is narrow due to the toxic effect of hazardous elements (Basu et al., 2009; Blissett and Rowson, 2012). The concentrations of PHEs in ashes (Figure 1) as well as ER and REI values (Table 4) are not in threat levels. Additionally, among them Cu, Mn, and Zn which have comparatively higher concentration are considered as micro-nutrients for plant growth. Therefore, thermal power plant ashes may possibly have little negative impact and may securely be applied in agricultural field (Basu et al., 2009). About 25 percent of produced fly ashes in India are utilised in construction sector like cements production, brick, tiles, etc. (Verma et al., 2015; Saha et al., 2019). Combustion ashes are abrasive and refractory in nature. This pozzolanic material containing silicon and aluminium forms cementitious product at ambient temperature together with calcium and water (Basu et al., 2009; Ahmaruzzaman, 2010). This pozzolanic nature along with lime binding property makes the fly ash suitable for cement production (Blissett and Rowson, 2012). The chemical character (Figure 5) of the studied ash reflects that these combustion residues can be used as raw material in the cement industry. Ash containing Si, Al, Ca, and Fe oxides are utilised as low-cost material in ceramics industry for the manufacture of brick, tiles etc (Basu et al., 2009; Blissett and Rowson 2012). Silica or quartz (Figure 5) is supplied as sand and are used to glazing and stiffening the ceramic body. Therefore, silica-based ashes are potentially used in ceramic trade (Ahmaruzzaman, 2010). Recently, fly ash has been used as a catalyst in industries because it contains various metal oxides (Figure 5) and has strong thermal stability (Basu et al., 2009). Some other potential application of fly ashes is base material for road and pavement in different layers (Blissett and Rowson, 2012). This improves the hardness and strength of the low-quality material mixed with ashes (Blissett and Rowson, 2012; Ahmaruzzaman, 2010). These are also utilised in coastal regions; embankments; and decorative purpose in the lakes, gardens, and parks (Basu et al., 2009; Ahmaruzzaman, 2010). Combustion ashes are also widely used in zeolite, geopolymer synthesis, filling of low lying area and mine as well as low cost adsorbent for removal of pollutant from air and water (Vejahati et al., 2010; Markwiese et al., 2014). One of the environmental crises of ash utilisation is the leaching of hazardous elements into the underlying water and soil (Rowe et al., 2002; Saha et al., 2019). The studied ashes have low content of hazardous elements (Figure 1) and can be satisfactorily recycled in the different fields (Basu et al., 2009; Blissett and Rowson, 2012). However, analysis and pre-treatment before each recycle is a primary task for eco-friendly utilisation (Blissett and Rowson, 2012; Bhattacharyya et al. 2009).

Treatment of ash before utilisation is crucial to resist the contamination of hazardous elements (Markwiese et al., 2014; Saha and Roychoudhury, 2019). Chemical treatment by stabiliser is useful for rendering the hazardous elements into the ash and reduction of the mobility of these elements into the soil and water (Bhattacharyya et al. 2009). Heavy metals can also be recovered from ash by extraction technique using water, acidic solutions, and micro-organisms (Basu et al., 2009; Blissett and Rowson, 2012). Thermal treatment and solidification may be applied for detoxifying the ashes and reuse in suitable manner (Bhattacharyya et al. 2009).

4. Conclusion

The feed coals of thermal power plants are high volatile bituminous to sub-bituminous in rank with a high ash yield (31.26-37.52%) and low moisture content (4.28-6.45%). Mineralogical analysis shows that coals are enriched with various minerals quartz, kaolinite, illite, dolomite, apatite, calcite, rutile, pyrite, and siderite. SiO_2 has a high concentration followed by Al_2O_3 and Fe_2O_3 relative to the other analysed major oxide elements TiO_2 , P_2O_5 , MgO , CaO , Na_2O , K_2O , and SO_3 . A few potential hazardous elements (PHEs) As, Sb, Cu, Mn, and Zn occur in coal and coal combustion residues (fly and bottom ash). Hierarchical cluster analysis predicts that Cu, Mn, and Zn have strong associations with ash forming elements (SiO_2 , Al_2O_3 , Fe_2O_3) but other two chalcophile elements, As and Sb, shows weak association with these major oxides. The calculated enrichment ratio (ER) and relative enrichment index (REI) values shows that Cu, Mn, and Zn are enriched both on to the fly and bottom ash. This capturing capacity of these elements varies with their content, occurrence, volatility and morphology of the combustion residues. Alternatively, the depletion of As and Sb in the ash supports their emission into the atmosphere during combustion. The water leachate concentrations of all the analysed elements are $\mu\text{g}/\text{kg}$ in range. A very feeble concentration is observed in case of As and Sb by laboratory water leaching experiment from fly and bottom ash. However, Mn and Zn have notable gradient nature from both combustion residues. Only Cu shows comparatively higher water leachate concentration in fly ash than bottom ash. The gradient natures of these elements are controlled by concentration, mode of occurrence into the ashes along with physical and chemical nature of solvent and ashes. The bio-availability test was performed in HCl medium to understand the impact of the PHEs in the living system. Though the range of concentration of all the analysed elements is also in $\mu\text{g}/\text{kg}$ range however, it is a concern for human health hazards. The prolonged uptake of these hazardous elements may cause several diseases. Therefore, contaminations of the hazardous elements are reduced by suitable ash disposal management and recycle. The combustion residues of the studied thermal power plants are fit for utilisation in various sectors like construction, geotechnical, and even in agricultural fields. Chemical characterisation of ashes by scanning electron microscope, leaching experiments, and calculated enrichment ratio (ER) and relative enrichment index (REI) values supports attentive recycling in several sectors to generate clean energy from coal combustion. An examination of ashes is necessary to select the proper reuse of ashes to avoid any possible contamination and application of pre-treatment as and when required for safe environment.

Declarations

Author's contribution statement: Debasree Saha collected the samples and analyzed the data as well as conceptualized the idea, framework of the research and wrote the manuscript; Tarit Roychowdhury supervised the research work and investigated all the nitty-gritty details of the study.

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Data availability: The author's have measured all the data used in this study and is duly quoted with this manuscript.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

Ethical statement: We, the authors, declare that we have stringently followed all the rules, and all the accepted principles of ethical and professional conduct have been followed. While carrying out the present research, no living entity were harmed or used as subjects of experiment. There was no involvement of human beings in this research and hence there is no question of sharing any private or personal information without informing the persons concerned. We also declare that the authors have strictly complied with the authorship principles furnished by the journal.

Consent: The authors have provided consent to communicate the manuscript to the “Environmental Science and Pollution Research,” and the institutions of the authors have no objection in this regard.

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Figures

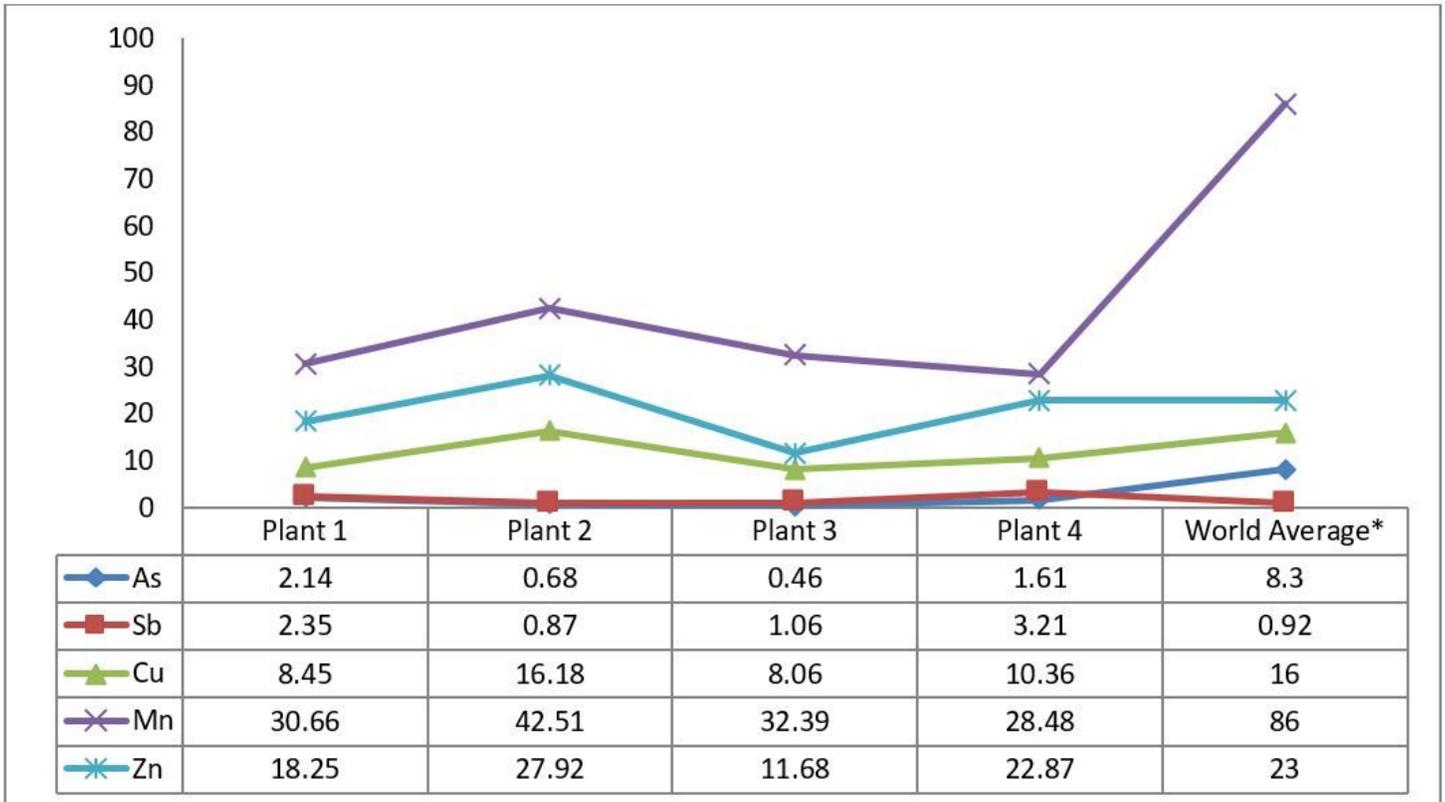


Figure 1

Average concentration ($\mu\text{g/g}$, air dried basis) of trace elements in coal

World Average* value of trace elements in coal reported by Ketris and Yudovich, 2009

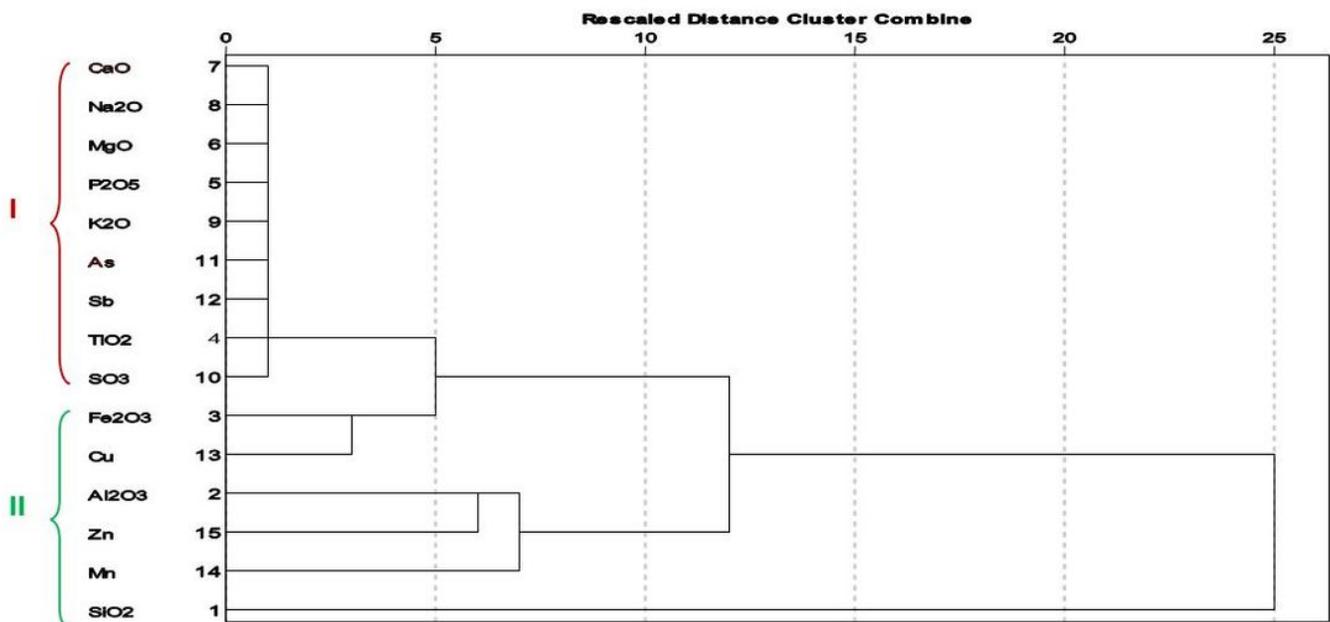


Figure 2

Association of PHEs with major elements oxides in coal

R mode hierarchical cluster using Euclidean distance in the dendrogram

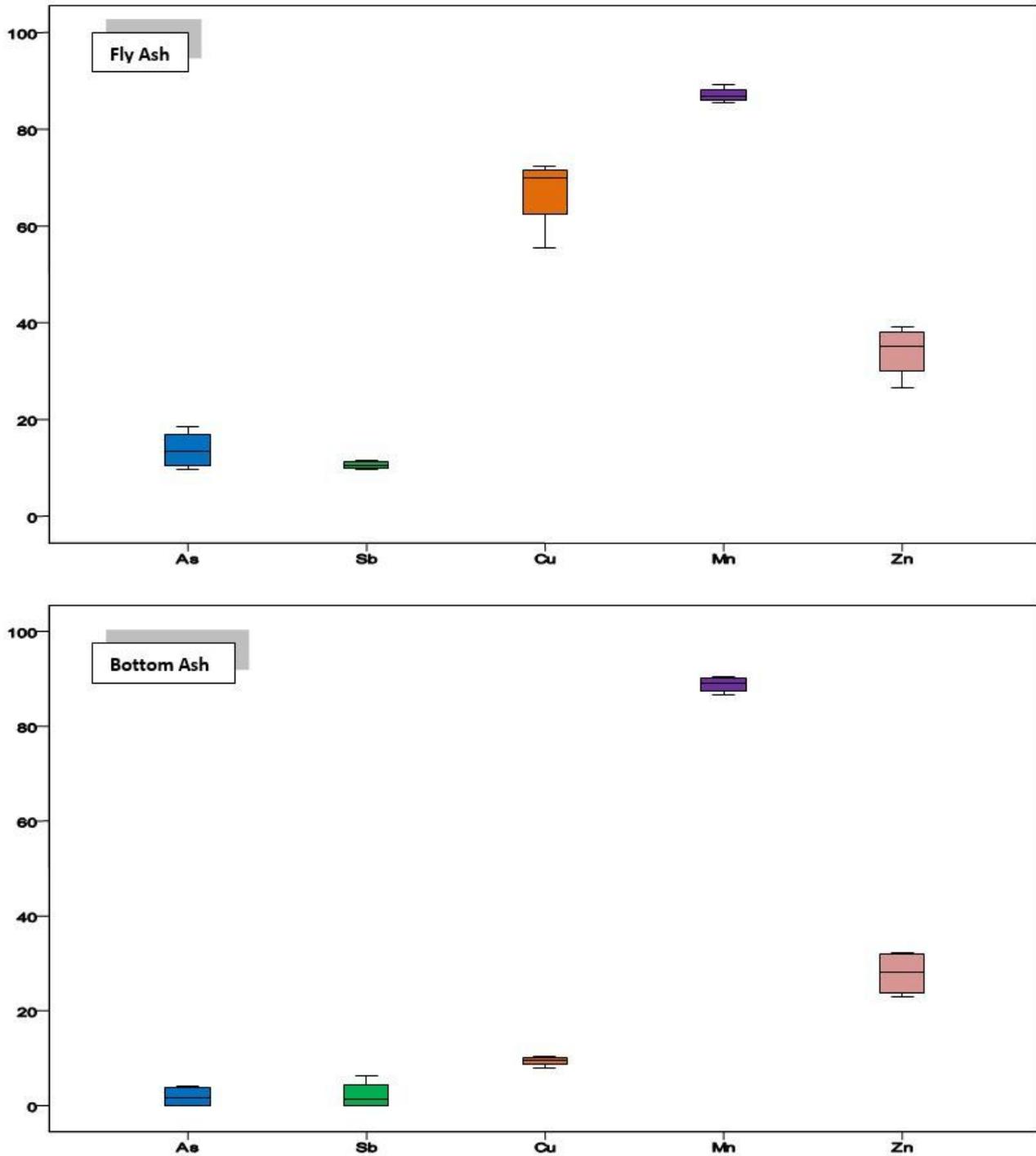


Figure 3

Water leachate concentration ($\mu\text{g}/\text{kg}$) of trace elements from coal combustion ash

In each box plot the median (middle line of box), 75% quartile (upper side of box), 25% quartile (lower side of box), minimum (lower whisker) and maximum (upper whisker) are depicted.

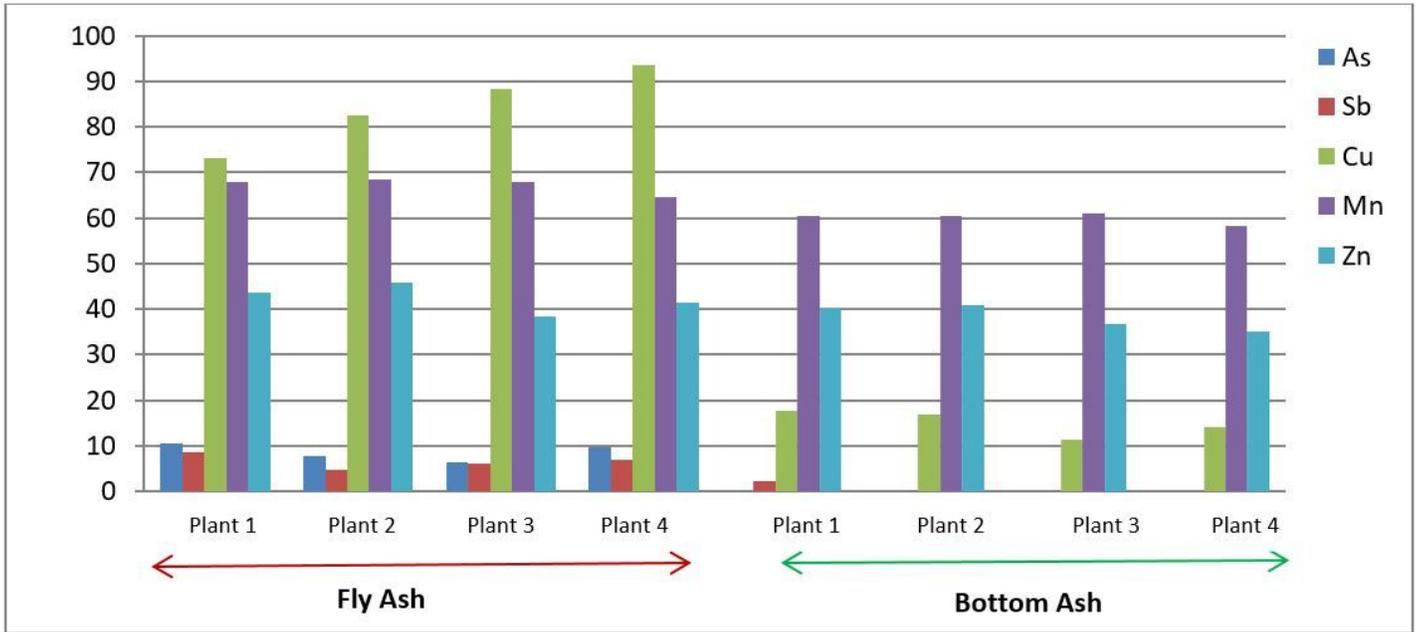


Figure 4

Concentration ($\mu\text{g}/\text{kg}$) of trace elements from coal combustion ash in bio-availability leaching test

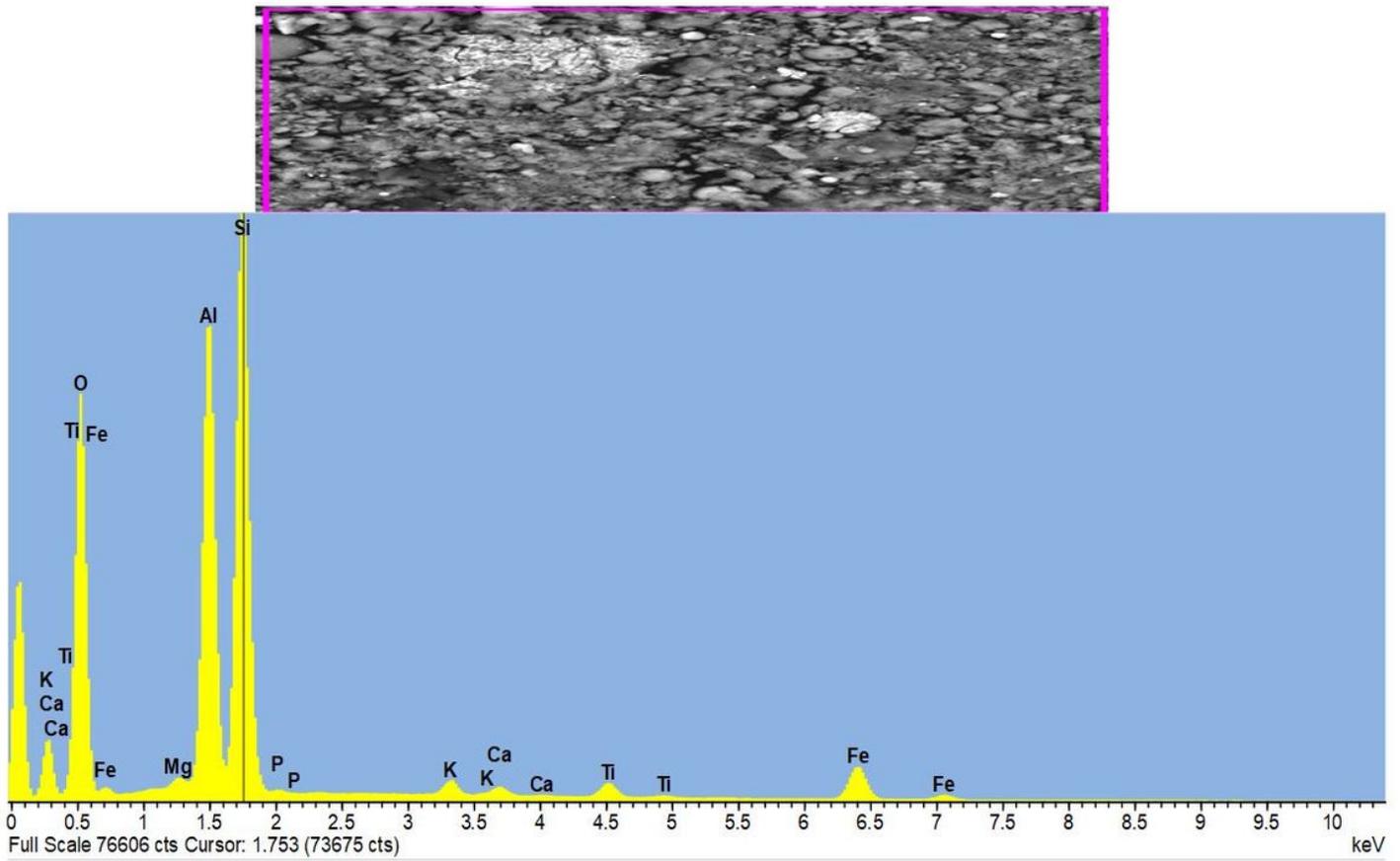


Figure 5

Elemental mapping of coal combustion ash by scanning electron microscope