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# Monitoring of arsenic fate with proximate parameters and elemental composition of coal from Thar coalfield, Pakistan



Jamshed Ali<sup>a</sup>, Tasneem G. Kazi<sup>a,\*</sup>, Jameel A. Baig<sup>a</sup>, Hassan I. Afridi<sup>a</sup>, Mariam S. Arain<sup>a</sup>, Naeem Ullah<sup>a</sup>, Sadaf S. Arain<sup>a</sup>, Saima Siraj<sup>b</sup>

<sup>a</sup> National Center of Excellence in Analytical Chemistry, University of Sindh Jamshoro, 76080, Pakistan

<sup>b</sup> Department of Information Technology, Quaid-e-Awam, University of Engineering Science and Technology, Pakistan

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### ABSTRACT

It was extensively studied that combustion of coal for power generation is an important anthropogenic contributor of toxic elements to the environment. In present study the exposure of arsenic (As) from coal samples collected from two sites (III and V) of Thar coalfield before and after burning were evaluated. Meanwhile the proximate parameters and elemental composition of collected coal samples were also studied in detail. The quantitative analysis of As in coal samples and their ash were achieved by microwave-assisted acid digestion methods prior to analyze by MHS-15 hydride generation atomic absorption spectrometry. The contents of As in coal samples of site-III of Thar coalfield was found to be higher as compared to site-V, it may be due to difference in geochemical mineral composition. The resulted data of ash indicated that during combustion of coal >88.5% of As can be released into the atmosphere. The evaluated moisture contents in coal samples of Thar coalfield indicated that the direct use of coal is not suitable for power generation and other activities.

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# 1. Introduction

Nowadays, Pakistan is facing energy crises due to unusable natural energy resources even in the presence of its huge amount. With grace of Almighty Allah, Pakistan has the largest natural lignite coal depositions in district Tharparkar, Sindh, Pakistan (Imran et al., 2014; Khurshid et al., 2013; Rafique et al., 2008; Tahir and Rauf, 2006). However, coal is one of the most important energy resources in developing countries (Liu et al., 2000). Unfortunately, explored coal in Pakistan has not been properly developed for power generation due to insufficient financing and lack of technological and human recourses (Gunter et al., 1997; Siddiqui, 2007). At the movement, the Government of Pakistan is focused on foreign private investors for the development of coal mining and application of it as a cheap indigenous energy resource (Zaigham, 2003; Zaigham and Nayyar, 2005). The use of coal for power and heat generation can produce significant amounts of toxic elements such as arsenic, mercury and other toxicants (Matschullat, 2000). The high contents of As in coal was also reported by other workers, which is considered to be a serious matter of concern for scientific community (Gemici et al., 2008; Imran et al., 2014; Keimowitz et al., 2005). The burning of coal is also highlighted

\* Corresponding author.

as a cause of As contamination of surface and groundwater in different areas (Singh et al., 2012; Tuzen et al., 2010).

The As in coal occurs in two major forms, bounded with organic and inorganic phases as oxygenated sulfide complexes (Guo et al., 2004). During coal combustion, As can vaporize and condense homogeneously/ heterogeneously to adsorb on the surface of fine fly ash particles (Vejahati et al., 2010; Yan et al., 2000). The As released into the environment due to burning of coal, may be responsible to create several kinds of health consequences (Larios et al., 2012; Melamed, 2005; Morin and Calas, 2006). It was studied that the coal mining activities create environmental health impacts. (Li et al., 2011). The main task of a hydrogeochemical study is to identify the process responsible for the evolution of As.

The present study has been carried out for the first time on Thar coalfield, where the open pit coal mining will be started soon with the collaboration of Australian Engineering company and Engro chemical (Pvt. Limited) Pakistan, whereas preliminary operational condition of underground coal gasification is in progress. A systematic work is urgently needed to understand the composition of coal in newly developed mining area of Pakistan, as well as the fate of As following environmental release.

In the present study, the content of As in coal and its residual ash samples were obtained from two sites, at four different depths of Thar coalfield (a largest natural coal basin of Pakistan), to check the available and exposure route of As into the environment. The As in coal samples and their ash were extracted by acid digested in a microwave oven. The proximate parameters (sulfur, moisture and ash) and elemental composition of coal samples were also analyzed. The correlation between different elements and As in coal samples has been studied.

*E-mail addresses:* ajamshed75@yahoo.com (J. Ali), tgkazi@yahoo.com (T.G. Kazi), jab\_mughal@yahoo.com (J.A. Baig), hassanimranafridi@yahoo.com (H.I. Afridi), mariamshahzadi29@yahoo.com (M.S. Arain), naeemullah433@yahoo.com (N. Ullah), ssadiashafi@gmail.com (S.S. Arain), Saimasiraj@quest.edu.pk (S. Siraj).

The accuracy of the methodology has been validated by the standard addition method. The concentrations of As in coal samples before and after burning were measured by MHS-15 hydride generation atomic absorption spectrometry (HG-AAS).

## 2. Materials and methods

# 2.1. Description of study area

Thar coalfield is located in the south-eastern part of Sind province in Pakistan on the stable western margin of the Indian plate and positioned between 24°45′–24°80′ N and 70°05′–70°30′ E as shown in Fig. 1 (Ali et al., 2015). The study area has a tropical desert climate (Imran et al., 2014). The temperatures during summer and winter remain between 24°C to 48°C and 9°C to 28°C respectively, rainfall varies from year to year, but average annual rainfall is 200 to 300 mm.

The geological survey of Pakistan has discovered a huge deposit of coal in 1992 at Thar during the research program assisted by United States geological survey. The Thar coalfield is spread over an area of more than 9100 km<sup>2</sup> with dimensions of 140 km (north–south) 65 km (east–west) with estimated reserves of 175 billion tones. (Ali et al., 2015). Thar coalfield is divided into twelve blocks according to the private power and infrastructure board, federal ministry of water and power government of Pakistan. The number of coal seams varies from hole to hole, and a maximum of 20 seams have been logged in some of the drill holes. The thickness of coal seams varies from 0.20 to 22.8 m.

Thar coalfield is covered by dunes with an average depth varying from 14 to 93 m. At the depth of >275 m the basement rock is generally granite (Fig. 2). The granitic rocks of the Thar coalfield may belong to the

proterozoic malani magmatism of western Rajasthan, India (Ahmad and Chaudhry, 2007). The basement rocks comprised of epidote amphibolite facies of metamorphic rocks ranging from mafic to granite composition. The kaolin deposits are generally covered by thick sand dunes and alluvium extending down to an average depth of 30 m. The depth of the kaolin pockets is estimated to be 2 to 8 m below the surface (Naseem et al., 2010). The paleocene-ecocene coal bearing horizons of claystone, carbonaceous claystone, sandstone and siltstone occur with interlaminated coal beds shown in Fig. 2. The sandstone is very fine to coarse grained and consists of ferromagnesium mineral grains. The met basalts are medium to coarse grained volcanic and plutonic rocks that have metamorphosed to epidote amphibolites and contain acidic dykes of rhyolite to quartz trachyte composition (Naseem et al., 2010). The coal bearing horizon of the Paleocene-Eocene sediments above the basement complex is designated as baraformation and has highly altered kaolinite (Choudry et al., 2010; Malkani, 2012). It was reported in literature that geoelectrical drilling and geophysical log data indicate four major divisions of lithological sequences in the whole Thar coalfield shown in Fig. 2. These zones are sand dune, sub-recent deposits, coalbearing formations of Paleocene, igneous and bfement complex of Precambrian age (Rafique et al., 2008; Zaigham, 2003).

### 2.2. Sampling

For the current study, coal samples were collected from four coal seam (n = 5 per seam) of each sites-III (n = 20) and V (n = 20), with the assistance of the Sindh coal authority. The drilling of the coal-field in site-III and V occurred at the time of sampling in 2014. The coal samples were collected by using core sampling method at different depths, ranging from 120 to 280 m. The collected coal samples were



Fig. 1. Study map of blocks-III and V (black shaded), Thar coalfield, Pakistan.



Fig. 2. Sedimentary column of the Thar coalfield, showing lithological characteristics of coal, coal seam and aquifer water.

subsequently transferred to clean polypropylene bags. On returning to the laboratory, each coal sample was spread on the plastic trays in fume cupboards and allowed to dry at ambient temperature for eight days. The samples were prepared by grinding and screening through 100-mesh sieve. To avoid contamination and weathering, all samples were stored in plastic bags marked with identity numbers.

### 2.3. Reagents and glassware

Ultrapure water (resistance 0.05  $\mu$ S/cm) obtained from an ELGA laboratory water system (Bucks, UK) was used throughout the experiments. The concentrated HCl (purity 37%, Sp.gr: 1.19), HNO<sub>3</sub> (purity 65%, Sp.gr: 1.41) and H<sub>2</sub>O<sub>2</sub> (purity 30%, Sp.gr: 1.11) were of analytical reagent-grade obtained from Merck, (Darmstadt, Germany). The working standard solutions for calibration were prepared using certified stock standard solution of As (1000 mg/L), Fluka Kamica (Bushs, Switzerland), the working standards were prepared by appropriate dilutions with 1.0 mol/L HNO<sub>3</sub>, whenever required. Solution of reducing agents, 3% (m/v) sodium tetrahydroborate (NaBH<sub>4</sub>) powder acros organics (New Jersey, USA) in 0.05 mol/L KOH were prepared freshly and filtered before use. All glass wares and polyethylene bottles were thoroughly vashed then soaked overnight in 5 mol/L HNO<sub>3</sub> and was thoroughly rinsed with distilled and de-ionized water before use.

### 2.4. Instrumentation

An end-over-end mechanical shaker (Gallankamp, Germany) was used for shaking. The phase separation was performed by centrifuge ROWKA Laboratory type WE-1, nr-6933 (Mechanika Phecyzyjna, Poland). A domestic microwave oven PEL, (Osaka, Japan), programmable for time and microwave power from 100 to 900 W, was used for total digestion of coal and ash samples. A pH meter (Ecoscan Ion 6, Kuala Lumpur, Malaysia) was employed for pH adjustments. The elemental composition of coal was carried out by energy dispersive spectroscopy EDS, (XFlash-4010) mount on the scanning electron microscope (SEM, FEICo, Hillsboro, USA). The concentration of As in all subjected samples was determined by a double beam Perkin Elmer model A Analyst 700 (Norwalk, CT, USA) atomic absorption spectrophotometer, equipped with a MHS-15 hydride generation system. The operating parameters for working of As hollow cathode lamp were set as recommended by the manufacturer. The operating conditions for determination of As by HG-AAS were shown in Table 1 and also described in our previous papers (Shah et al., 2009; Tuzen et al., 2009).

### 2.5. Proximate parameters of coal

The proximate parameters i.e. (sulfur, moisture and ash) of coal samples (triplicate of each) collected from four depth of two sites were performed by standard methods. The pH values were determined, using a ratio of 1:2.5 (coal and ultrapure water), according to the official

#### Table 1

Experimental condition for arsenic measurement in coal and ash samples by HG-AAS.

Parameters	Arsenic
Lamp current	10 mA
Wave length	193.7 nm
Slit-width	0.7 nm
Oxidant (air)	17 L/min
Fuel (acetylene)	2.2 L/min
Atomization site	Pre heated quartz tube atomizer (QTA)
Pre-reaction purge time	20 s
Post-reaction purge time	30 s
Sample volume	10 µL
Carrier gas	200 mL/min
Background correction	$D_2$ Lamp

Keys: mA = milliampere, nm = nanometer, L/min = liter/min, s = second,  $\mu L = microliter$  and  $D_2$  Lamp = Deuterium lamp.

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# Table 2 Validation of methodology by standard addition method for arsenic in real samples of coal

and their ash of Thar coalfield.									
I.D	Added As (mg/L)	As in coal		As in ash					
		$Mean\pmSD$	%R	$Mean\pmSD$	%R				
$(S_3^{III})$	0	$30.2\pm0.21$	-	$2.82\pm0.19$	-				
	2.5	$32.6\pm0.18$	96.0	$5.31\pm0.16$	99.6				
	5	$35.1\pm0.15$	98.0	$7.79 \pm 0.28$	99.4				
	10	$40.1\pm0.19$	99.0	$12.8\pm0.32$	99.8				
$(S_3^V)$	0	$19.7\pm0.60$	-	$1.73\pm0.06$	-				
	2.5	$22.2\pm0.51$	100	$4.17\pm0.19$	97.6				
	5	$24.6\pm0.65$	98.0	$6.68 \pm 0.26$	99.0				
	10	$296 \pm 0.82$	99.0	$118 \pm 0.42$	98 7				

Key: SD = Standard deviation.

% R = percentage recovery.

methods of soil analysis (Jamali et al., 2008). Moisture content in coal samples was determined by standard method (Evans, 1978), coal samples dried to a constant weight in an electric oven (Suszarka laboratoryjne, Poland) at  $110 \pm 5$  °C and the percentage of water loss was calculated (Shah et al., 2009).

### 2.6. Preparation of ash samples

The ash content was measured by ASTM standard test methods (Sluiter et al., 2008). Weighed 5.0 g of duplicate of each coal samples in crucibles and placed in a muffle furnace, then heated up to 800 to 900°C for 6 h with stepwise increase in temperature. During ashing process a significant amount of air should have access to the furnace. The specific energy of coal is dependent on composition of coal, moisture and ash content. The percentage ash was calculated by using the following formula.

$$\%Ash = \frac{Weight of coal residue after buring}{Weight of coal before burning} \times 100$$

### 2.7. Total As contents in coal and ash samples

The concentration of As in coal and remaining residual ash samples were extracted using microwave-assisted acid digestion procedure. Triplicate samples of coal samples and their corresponding ash of each site were directly weighed into the 25 mL flasks separately and placed in a polytetrafluoroethylene flask. The 2 mL of acid oxidant mixture (HNO<sub>3</sub>:HF at 2:1 ratio) was used and all flasks were kept at room temperature for 2 h. Then the flasks were placed in domestic microwave oven (PEL PM 023) programmable for time, with microwave power from 100 to 900 W, and heated at 80% of total power, for 15 min. After cooling, the sample digests were diluted with ultrapure water and filtered through Whatman 42 filter paper, transferred into a 25 mL flask, and brought to volume with ultrapure water. Analytical blanks were prepared in the same way, without addition of any sample. The

As contents in acid digested coal and their ash samples were determined by HG-AAS. For validation of methodology, standard addition method was used, in order to determine the As contents in real coal and ash samples due to the unavailability of a certified reference material of coal and ash. Three replicate subsamples of a coal collected from sites III and V of the Thar coalfield were spiked with three known concentration levels of As standards.

### 2.8. Analytical figure of merits

The calibration graph for analysis of As standards was prepared from 1.0 to 20 µg/L, while the coefficients of correlation for HG-AAS technique was found to be 0.996. The detection and quantification limits were given by LOD =  $3 \times$  SD/m and LOQ =  $10 \times$  SD/m, respectively, where SD is the standard deviation of ten measurements of a reagent blank and m is the slope of the calibration graph. The LOD for HG-AAS was 0.0248 µg/g while the LOQ was 0.0827 µg/g, respectively. The % recovery was observed >97 by using standard addition method in coal and their ash samples shown in Table 2.

### 3. Results and discussion

### 3.1. Proximate characteristics of coal

The total As contents in coal and their ash and proximate parameters (pH, sulfur, moisture and ash) are shown in Table 3. The pH values of collected coal samples of site-III and V were found in the range of 3.51 to 5.93 (Table 3). The chemical nature of arsenic compounds, in particular their tendency to change valence states or chemical form under a wide range of pH and redox conditions, makes it difficult to assess their fate and mobility in the environment (Yudovich and Ketris, 2005). The moisture contents of coal samples of Thar coalfield were observed in the range of 30.9 to 47.2% (Table 3). The total moisture in coal includes the inherent and surface moisture, which affects the calorific value and the concentration of other constituents. The coal ashes are the residues of organic and inorganic substances left after its combustion at high temperature. The ash contents of Thar coal varied from 5.85 to 10.5%, obtained after heating at 800°C to 900°C (Table 3).

### 3.2. Total As content in coal and ash samples

The total As values in 40 representative coal samples collected from four different depths of sites-III and V, ranged from 26.2 to 30.8 and 18.0 to 22.2 mg/kg respectively shown in Table 3, these values are consisted with other study (Wang and Mulligan, 2006). The As contents increased with the increase of depths in site-III but the pattern was different for site-V, indicating a decreasing order as  $S_1 > S_3 > S_4 > S_2$ . The correlation of depths with As concentration in coal samples of site-III was significantly higher (r = 0.98; p < 0.05) as compared to sampling sites-V (r = 0.69; p > 0.05). The contents of As and related volatile compounds are mobilized during coal combustion and enter into the environment

Table	- 3
Table	

Resulted data of As contents in coal and their ash samples, along with proximate parameters of coal.

Sites	I.D	Depth (m)	рН	Sulfur (%)	Moisture	Ash (%)	Total As contents in (mg/L)		
					(%)		Coal ash		% EE
III	S <sub>1</sub> <sup>III</sup>	130-145	$(5.14 \pm 0.81)$	$(1.53 \pm 0.48)$	$(32.3 \pm 0.23)$	$(7.77 \pm 0.54)$	$(26.2 \pm 0.16)$	$(2.60 \pm 0.19)$	90.1
	$S_2^{III}$	165-180	$(5.32 \pm 0.14)$	$(0.80 \pm 0.23)$	$(39.6 \pm 0.23)$	$(8.64 \pm 0.36)$	$(28.0 \pm 0.80)$	$(2.52 \pm 1.29)$	91.0
	S <sup>III</sup>	200-210	$(4.98 \pm 0.06)$	$(1.12 \pm 0.48)$	$(47.2 \pm 0.08)$	$(9.32 \pm 0.31)$	$(30.2 \pm 0.44)$	$(2.82 \pm 0.08)$	90.7
	S <sup>III</sup>	245-255	$(5.88 \pm 0.50)$	$(1.08 \pm 0.41)$	$(46.9 \pm 1.53)$	$(10.5 \pm 0.13)$	$(30.8 \pm 1.16)$	$(3.16 \pm 0.10)$	89.7
V	$S_1^V$	125-135	$(5.03 \pm 0.92)$	$(1.62 \pm 0.76)$	$(31.4 \pm 0.15)$	$(6.60 \pm 0.85)$	$(22.2 \pm 0.02)$	$(2.47 \pm 0.19)$	88.9
	$S_2^V$	160-165	$(5.93 \pm 0.04)$	$(0.60 \pm 0.33)$	$(39.7 \pm 0.03)$	$(5.85 \pm 0.44)$	$(18.0 \pm 0.80)$	$(2.06 \pm 1.29)$	88.6
	S <sub>3</sub> <sup>V</sup>	170-175	$(3.51 \pm 0.04)$	$(0.49 \pm 1.11)$	$(33.6 \pm 1.54)$	$(8.8 \pm 0.17)$	$(19.7 \pm 0.60)$	$(1.73 \pm 0.06)$	91.2
	$S_4^V$	185-205	$(5.62 \pm 0.04)$	$(0.80 \pm 0.44)$	$(30.9 \pm 0.90)$	$(7.70 \pm 0.57)$	$(18.2 \pm 1.16)$	$(1.40 \pm 0.16)$	92.3

Key: %EE = Percentage environmental exposure.



Fig. 3. a: The spectra of EDS for elemental composition of coal sample of site-III. b: The spectra of EDS for elemental composition of coal sample of site-V.

as gas or solid particles, depending on the burning conditions (Yudovich and Ketris, 2005).

The As in residual ash was indicates the behavior of As in terms of its mobility and consequent environmental concerns after combustion (Finkelman et al., 2002; Wang and Mulligan, 2006). The As contents in residual ash of coal samples collected from two sites at four different depths, site-III corresponding to  $S_{11}^{II}$ ,  $S_{21}^{II}$ ,  $S_{31}^{II}$ ,  $S_{31}^{II}$  (2.19 to 3.00, 1.79 to

3.26, 2.77 to 2.9 and 3.01 to 3.24) mg/kg and site-V as  $S_1^V$ ,  $S_2^V$ ,  $S_3^V$ ,  $S_4^V$  (1.33 to 1.60, 1.14 to 2.96, 1.65 to 1.80 and 1.27 to 1.59) mg/kg, respectively. The resulted data indicate that during combustion >88.5% of the total As might be released into the atmosphere (Table 3). It is considered that during the combustion of coal, the organic matter is combusted and only the inorganic matter remains in the coal ash. The same trend has been previously reported in the literature (Finkelman

Table 4

Analytical results of elemental composition in coal samples of two sampling sites of Thar coalfield at different seams.

Sites	I.D	% C	% O	% Na	% Mg	% Al	% Si	% Ca	% Fe
III	S <sub>1</sub> III	45.9-53.4	32.1-37.56	0.86-1.46	0.25-0.73	2.34-3.98	1.87-3.52	0.47-1.72	0.52-2.57
		$49.7\pm4.98$	$34.8 \pm 3.18$	$1.16\pm0.30$	$0.49\pm0.15$	$3.16 \pm 1.22$	$2.69 \pm .61$	$1.10\pm0.48$	$1.54\pm0.35$
	$S_2^{III}$	47.8-57.3	33.8-38.6	0.63-1.37	0.21-0.62	1.03-2.94	0.96-1.72	0.41-1.83	0.33-1.92
		$52.6\pm5.04$	$36.2 \pm 3.40$	$1.00\pm0.28$	$0.41\pm0.15$	$1.98\pm0.41$	$1.34\pm0.2$	$1.12\pm0.54$	$1.12\pm0.43$
	$S_3^{III}$	49.1-58.1	39.0-45.1	0.62-1.07	0.30-0.36	0.83-1.62	0.74-1.52	0.40-1.22	0.90-1.50
		$53.7\pm5.00$	$41.9 \pm 3.07$	$0.84\pm0.23$	$0.33\pm0.02$	$1.23\pm0.44$	$1.13\pm0.43$	$0.80\pm0.44$	$1.05\pm0.40$
	S <sub>4</sub> <sup>III</sup>	50.6-59.6	38.3-43.7	0.45-0.78	0.09-0.20	0.55-1.06	0.38-0.78	0.45-1.31	0.35-1.25
		$55.2 \pm 5.12$	$40.9\pm2.97$	$0.61 \pm 0.17$	$0.14\pm0.04$	$0.80\pm0.29$	$0.58\pm0.22$	$0.88\pm0.49$	$0.85\pm0.48$
V	$S_1^V$	32.5-43.4	48.3-48.4	0.97-1.39	0.27-0.42	2.53-4.26	1.90-3.33	0.28-0.70	0.71-2.46
		$38.0 \pm 7.70$	$48.4\pm0.06$	$1.18\pm0.30$	$0.34 \pm 0.11$	$3.40 \pm 1.22$	$2.62 \pm 1.01$	$0.49\pm0.23$	$1.58 \pm 1.24$
	$S_2^V$	54.1-63.1	34.5-39.4	0.75-1.23	0.24-0.42	0.29-0.56	1.05-2.10	0.59-1.68	0.20-1.53
		$58.6 \pm 6.37$	$36.9 \pm 3.46$	$0.99\pm0.34$	$0.33 \pm 0.13$	$0.42\pm0.19$	$1.67\pm0.57$	$1.14\pm0.77$	$1.35\pm0.18$
	$S_3^V$	52.2-61.8	35.2-39.6	0.54-0.88	0.25-0.50	0.98-1.87	0.74-1.47	0.39-1.11	1.09-1.42
		$57.0\pm6.80$	$37.4 \pm 3.12$	$0.71\pm0.24$	$0.37\pm0.09$	$1.42\pm0.63$	$1.11\pm0.52$	$0.75 \pm 0.51$	$1.23\pm0.12$
	$S_4^V$	50.1-59.3	38.5-43.3	0.58-0.94	0.09-0.16	1.00-2.21	0.80-1.67	0.64-1.80	0.29-1.13
		$54.7\pm6.50$	$40.9\pm3.42$	$0.76\pm0.26$	$0.12\pm0.05$	$1.57\pm0.5$	$1.23\pm0.42$	$1.22\pm0.82$	$0.71\pm0.59$

### Table 5

Correlation coefficient and p values in p	arenthesis for different elements in coal of Thar coalfield.
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Elements	С	0	Na	Mg	Al	Si	S	Ca	Fe
Oxygen Sodium Magnesium Aluminum	-0.96 (0.01) -0.70 (0.12) -0.46 (0.36) -0.88 (0.02)	0.56 (0.24) 0.27 (0.60) 0.77 (0.08)	0.87 (0.02) 0.641 (0.17)	0.38 (0.46)			-		
Silicon	-0.88(0.022)	0.79 (0.06)	0.56 (0.25)	0.24 (0.64)	(0.99) (0.00)				
Sulfur	-0.79 (0.06)	0.69 (0.13)	0.82 (0.04)	0.82 (0.04)	0.54 (0.26)	0.48 (0.34)			
Calcium	0.73 (0.10)	-0.65 (0.16)	-0.38 (0.46)	-0.07(0.90)	-0.94(0.01)	-0.96(0.00)	-0.24(0.66)		
Iron	-0.91 (0.01)	0.85 (0.03)	0.68 (0.13)	0.58 (0.22)	0.67 (0.15)	0.65 (0.16)	0.93 (0.01)	-0.43(0.40)	
Arsenic	-0.07 (0.90)	0.27 (0.61)	-0.33 (0.52)	-0.62 (0.19)	0.12 (0.82)	0.21 (0.70)	-0.46 (0.36)	-0.35 (0.50)	-0.27 (0.61)

et al., 2002; Wang and Mulligan, 2006). The environmental exposure of As during burning can be estimated by using formula.

$$\% EE = \frac{(As \text{ contents in coal} - As \text{ contents in Ash})}{(As \text{ contents in coal})} \times 100$$

## 3.3. Elemental characteristics of coal

The elemental composition of coal has been measured by energy dispersive spectrometry (EDS) as shown in Fig. 3a and b, and the average values are summarized in (Table 4). The percentage of carbon (C) in coal sample were found in the range of 38–58%, which is one of the major constituent of coal. It was reported that high percentage of C is characteristic of best quality of coal and enhance the coal rank (Li et al., 2011; Ward et al., 2008). The correlation study of elements in coal samples indicated that C has strong negative correlation with O, Fe, Na, S, Si and strong positive correlation with Al and Ca ( $r \ge 0.80$ ; p < 0.01) as shown in Table 5. The carbon content of a coal is essential for making mass of coke (Nasirudeen and Jauro, 2011).

The correlation study also identified that sulfur has a strong correlation with Na, Mg and Fe reflected the presence of typical authigenic minerals (calcite, pyrite, marcasite, gypsum). The resulted data indicated the low content of sulfur in coal samples of Thar coalfield, which indicated that the coal is good for fire or energy production. It was reported that the low S contents is a characteristic of coals formed under freshwater conditions (Li et al., 2011; Ward et al., 2008). The S, Ca, Na and Fe have weak correlation with As in coal samples of Thar coalfield (p > 0.1). Whereas, As has negative correlation with Mg (p < 0.5), which indicated the presence of Mg bearing mineral in coal samples of Thar coalfield (Table 5). It was reported that the oxides of Fe, Ca, Mg, and S, represent minerals such as Ca-Fe-Mg sulfates, Ca-Mg-Fe carbonates, which commonly have dominant origin in coal (Vassilev and Vassileva, 1996). It was reported that the alkali metal, Na, Al, Ca, free Al<sub>2</sub>O<sub>3</sub>, and other metals in burning gas of coal at <1800 °C, the As can react with sulfates, on the hot sides of the boilers fed by coals and a thick films appeared containing up to 25% As<sub>2</sub>O<sub>3</sub>. These films resulted in rapid corrosion of the steel pipes (Yudovich and Ketris, 2005).

### 4. Conclusions

The current study show that the >88.5% of As will expose to the environment during coal burning for power generation and other activities. The As bonded to volatile organic matter of coal during combustion may cause the environmental pollutions. The total contents of As in coal and their ash samples of site-V were lower as compared to site-III but the difference was not significant (p < 0.05). The resulted data indicated that the coal of newly developed Thar coalfield contained large contents of moisture, which may affect the boiler system to create difficulties for power generation during combustion. The ash contents of coal samples were obtained <10%, which indicated that the coal samples contain high percentage of moisture and volatile organic matters. The high percentage of C in coal samples indicates the good quality and also

enhances its rank. The coal samples of Thar coalfield contained less amount of sulfur as compared to other lignite coal in world. Thus, it can be recommended that underground coal gasification is the best choice for power generation. Moreover, it is least environmental pollution creating technique as compares to others.

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