

Arsenic Presence in Block I & II of Thar Coal Field: Coal Combustion Behavior of Thar Coal

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Abstract:

The aim of the current study is to evaluate the occurrence of arsenic in coal collected from Thar coalfield, Pakistan, and its behavior during the combustion. Fractionation of arsenic (As) in coal samples was carried out by Community Bureau of Reference sequential extraction scheme (BCR-SES) and single-step-based BCR method (BCR-SS). These methods are validated using the certified reference material of sediment BCR 701 and standard addition method. The stepwise fractions of (As) in laboratory-made ash (LMA) have been also investigated. The extractable (As) content associated with different phases in coal and LMA samples were analyzed by electro thermal atomic absorption spectrophotometer. The extraction efficiency of As by BCR-SS was slightly higher than BCR-SES, while the difference was not significant. The BCR-SS method is a time-saving method because it can reduce the extraction time from 51 to 22 h. The (As) contents in LMA revealed that during combustion of the coal, >76 % of (As) may be released into atmosphere. The relative mobility of (As) in the coal samples was found in increasing order as follows: oxidizable fraction < reducible fraction < acid soluble fraction. The total and extractable (As) obtained by BCR-SES and BCR-SS were higher in coal samples of block I as compared to block II.

Keywords: Thar coalfield Arsenic, Single and sequential extraction, Laboratory-made ash

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I. Introduction

Energy has become pertinent for international economy and development since the industrial revolution. To acquire the energy security, states pursue their defense and foreign policy accordingly. There are different sources to extract energy, some suitable for small scale and some suitable for large scale. Energy extraction though is expensive and lengthy process, survival without it is unavoidable. Recent shift of extracting energy from water and is to thermal especially with virgin coal lying on mountain areas of many unexplored areas.

Coal is one of the most important energy sources for power generation (Liu et al. 2000). Coal is one of the cheapest sources of extracting energy and converting it into electricity with some operating conditions and hazards with it. Pakistan has remained since long the in energy crises as of purchasing oil and running it as fuel to burn electricity is expensive for country like Pakistan. Though second largest coal field of the world after America resides untouched in Pakistan with capacity of not only generating electricity to fulfill country needs but also to supply to neighboring countries. Since last decade Pak-China collaboration on CPEC and different development projects has brought in the awareness of *Thar Coal Field* in Pakistan. The use of coal for power and heat generation can produce significant atmospheric emissions of toxic elements, such as arsenic, mercury, and other toxicants (Matschullat 2000). But proper investigation and extraction of coal from thar coal field can build a New Pakistan emerging through energy crises to infrastructural country.

Arsenic is a chemical element with the symbol (As) and atomic number 33. Arsenic occurs in many minerals, usually in combination with sulfur and metals, but also as a pure elemental crystal. Arsenic is a metalloid. Coal as a metalloid contains extent of Arsenic that in combustion process can be some time harmful for the eco system and can be hazardous for environment. Arsenic (As) in coal occurs in two major forms (AsIII) and (AsV) as oxygenated complexes, and it may also occur as sulfide (Guo et al. 2004). During coal combustion, (As) can vaporize and condense homogeneously to form submicron ash particles or heterogeneously to adsorb on the surface of fine fly ash particles (Yan et al. 2000; Vejehati et al. 2010).

The (As) from coal or fuel burning may be released into the environment and may cause several kinds of health consequences. The assessment of total As content in polluted environmental samples is a poor indicator of its bioavailability, mobility, and toxicity because each species of As have different properties, i.e., As5+ is less toxic as compared to As3+ (Huggins et al. 1993; Arain et al. 2008). Therefore, it is necessary to

determine its chemical forms associated with different phases of the coal and its ash along with the total (As) contents (Guo et al. 2004; Dai et al. 2012). The As in coal, soil, and rocks is partitioned into the different phases, i.e., organic matter, oxyhydroxides of iron, aluminum and manganese, phyllosilicate minerals, carbonates, and sulfides (Larios et al. 2012).

In addition, metal ions are retained on these solid phases by different mechanisms (ion exchange, outer and inner sphere surface complication (adsorption), precipitation, or co precipitation) (Ure and Davidson 2008). The sequential extraction schemes (SES) are well accepted methods to assess the chemical fractionation of the element in soil, rocks, sediment, and coal (Seames and Wendt 2000; Lombi et al. 2000; Keon et al. 2001; Wenzel et al. 2001; Izquierdo and Querol 2012). To standardize the different extraction schemes, the Community Bureau of Reference (BCR), now Standards, Measurements and Testing Programmed (SM&T), has proposed a three-step extraction scheme (Nyström et al. 2003). The environmental application of sequential extraction procedures provides valuable information. However, SES methods are tedious and time consuming and there is the possibility of read sorption and redistribution of (As) to different phases during the experimental work. To overcome these problems, SES methods are replaced with single-step extraction methods involving the same reagents and operating conditions as used in the original SES methods (Arain et al. 2008; Baig et al. 2009).

The principal aim of this study was to evaluate the different fractions of AS in coal samples of two blocks of the Thar coalfield using a conventional BCR sequential extraction scheme (BCR-SES). An attractive approach has been adopted by replacing the BCR-SES by BCR single-step (BCR-SS) extractions operating the same protocol and reagents as used in the BCR-SES. The accuracy of the proposed methods has been validated by the standard addition method and certified reference material of sediment (BCR 701). The extraction procedures were also applied to real coal samples of the largest natural coal basin of Pakistan, to check the available and mobile phase of As. Moreover, concentrations of different (As) fractions in the laboratory-made ash (LMA) were determined using sequential extraction scheme. The purpose of investigation is to highlight the amount or Arsenic presence in Thar Coal Field and combustion behavior of coal from coal field. Block 1 and Block 2 coal is sampled for investigation as block 3 and block 4 is under digging process.

1.2 Background

Thar Desert of district Tharparkar, Sindh Pakistan lies in the southeastern zone of Sindh situated at a distance of 380 km. from Karachi. It is bound on the eastern side by the border with India, in the North by districts of Mirpurkhas and Badin. The name “Thar” is derived from Thul the general term for the region. The land area of Thar is spread over about 4,791,025 acres, out of which 2,394,399 acres are cultivable. The south-eastern part known as Nagarparkar, consists of granite hills with plain cultivable lands, most of the desert consists of sand dunes with fl at plain between them where agriculture can take place. The main occupation of people is cattle and livestock rearing, which about 60% of their living derived. Crops are grown after rain and some handicrafts (carpet weaving, cloth weaving, embroidery, etc.) also flourish. Rain is the main source of water in Tharparkar arid region. It is very erratic and the annual rainfall varies from 0-300 mm. All agriculture and livestock activities are dependent on rainfall. The failure of monsoon would mean no agriculture crop and no fodder for the cattle and livestock.

The main crop of Thar is Bajra and Gawaar. In good rainy years, lintels, melons and sesame are also grown with main crop. The Thar Desert requires seasonal showers for vegetation, crops, animals and ‘Palaar’ (drinking water) and ‘toba’ (community water pool), but drought has continuously increased the misery of its inhabitants over the last 6/7 years. About 20% of rain water is wasted through seepage and another 40% is lost due to evaporation, as the sun is merciless with temperature often rising to 41°C, migration, which used to be seasonal is now becoming permanent as famine like situations develop regularly. According to a study by an NGO Thardeep currently there is 70% food deficit and half starved animals are being sold for subsistence.

It is sheer resilience, will power and the inner strength that is the hallmark of the average Thar that helps him to survive. A vast numbers still live in Jhuggies. Since November, 2001, Food for Walk, program is being implemented by NGO Baanh Beli in over a hundred villages with the assistance of World Food Program. This includes household water tanks at community points and 27 hand pumps provided by UNICEF. However, all this can only succeed, if the rains come. For digging as well, a man still has to be lowered by four men into a hole with a 4.f. radius. At present some of the problems of Thar, besides rain and water are: -

- Low on political priority
- Non-dissemination of information
- Lack of communication
- Infrastructure-roads/living places/proper transport
- Non-availability of modern technology, education.
- Non-availability of mining expertise, etc.
- Increase Socio-economic activities

- Develop communication system
- Establish TV and Radio Station
- Disseminate information regarding Thar coal
- See that investment is related to profit.
- Develop infrastructure allied business

II. Literature Review

Detrimental impacts of coal mining, coal combustion, and coal by-product disposal on the environment are well documented in scientific literature. They are mainly related to acid-mine (S) drainage problems (Burgos et al., 2012), selenium (Se) leaching from ash, and its concomitant mobility (Dreher and Finkelman, 1992; Harkness et al., 2016), and soil, air, and water pollution (Baruah et al., 2006; Oliveira et al., 2014; Saikia et al., 2015a; Nišiu et al., 2016). Unlike Croatia, coal petrology and coal geochemistry research in India is a very active scientific discipline, and one of the leading experts is Professor Prakash K. Singh (BHU), whose few latest papers are briefly introduced here. Singh et al. (2017b) adopted an integrated approach to study the lignite deposits of Surkha mine associated with the Khadsaliya Clays Formation (Eocene) of the Saurashtra Basin, in Western India. Organic petrographic, palynofacies and geochemical data of the sampled succession have been acquired and discussed. The dimethyl formamide, technical grade, obtained from du Pont de Nemours and Company, Inc., was dried with KOH following a procedure described by Sears et al. (1955). The coal used in the course of the preliminary investigation was prepared as follows. A fresh sample of approximately 20 kilograms of Illinois high-volatile B bituminous No. 5 Coal from Saline County, size 2 by 3 inches, was collected at the mine and sealed in an airtight container. On the basis of the factors governing the choice of solvent and the considerable amount of work published by Jones and Wheeler (1915, 1916) in which they claimed that the coking properties of coal depend on the presence of a pyridine soluble constituent, it was decided to choose pyridine as a solvent and to study the pyridine extracts and residues. The pyridine extracts were subsequently extracted with reagent grade chloroform, conforming to A. C. S. specifications, obtained from Merck and Company, Inc.

The chloroform extracts in turn were extracted with freshly redistilled pure grade normal-hexane obtained from Phillips Petroleum Company. To obtain a better basis for comparing yield of extraction, physical properties, and chemical nature of the extracts and residues, two coals of similar chemical composition and plastic temperature characteristics but of different maximum fluidities were chosen. The two samples were an Illinois high-volatile B bituminous No. 5 Coal from Saline County, and an Eastern high-volatile A bituminous Hinshaw Coal from West Virginia. The Illinois coal, size 2 by 3 inches, was taken fresh from the mine. The Eastern coal, size minus one-fourth inch, was obtained from a fresh shipment at a plant in St. Louis, Missouri. Both coals were prepared in the same manner described previously. In addition, the minus 40-mesh portions were screened to obtain minus 40- to plus 60-mesh stock samples. Such samples were not representative of the coals but were prepared specimens that permitted a better basis for comparison.

Half of the fresh Illinois coal minus 40- to plus 60-mesh stock sample was spread in a pan to a uniform depth not exceeding one-fourth inch and left in the air at 36°C until oxidation completely destroyed the plastic characteristics. A period of 45 days sufficed for this. Plasticity measurements of coal, extracts, and residues were made by a Gieseler plastometer (Soth and Russell, 1943). The instrument, as modified by Rees and Pierron (1954) and shown on plate 2, includes a fixed position for the thrust bearings in the head of the plastometer and provision for removal of the decomposition gases by suction.

Mahadevan (1929) was one of the first to study coal structure by the diffraction method. On the basis of similarity between data obtained from coal and data from graphite, he concluded that coal contains compounds having a hexagonal ring structure similar to that of graphite. Blayden et al. (1944) made detailed investigations of the x-ray patterns of coals, and compared the coal carbonization products with those of cellulose, lignin, and glycine. They also postulated a graphite-like structure for coal based on the fact that data indicated the presence of interplanar spacing $d(002)$ of the same order, 3.5 Å, as that between successive layers in a graphite crystal. In addition, they suggested other lamellar structures that could also stack with a distance of 4.5 Å, between layers. Nelson (1954), by using improved techniques, was able to calculate the statistical distribution of atoms around any arbitrary center in coal. Hirsch (1954) derived the average number of aromatic rings from the average diameter of the lamellae.

Whitaker (1955), in his review of the ultimate structure of coal, stated that although the x-ray methods allow deductions somewhat indirectly related to the structure, they allow no direct interpretations. This was probably because of the very diffuse nature of the halos produced by essentially non-crystalline solids, in comparison with sharply resolved peaks in diffraction patterns of crystalline solids. Nevertheless, if x-ray study shows the same trend or indication as do other techniques, its use may be justified. We therefore decided to obtain x-ray scattering data for each sample investigated by means of a General Electric Unit XRD-3, copper anode tube, Ni filter, 50KV-15 ma, equipped with a 1" slit and a .Zo screen.

1.4 Research Area (Block I and Block II)

Table 1 Research Blocks

S/No.	Name/Blocks	Area	Coordinates	
1	Sinhar Vikian Varvai, Block-I	122.00	24° 35'N to 24° 44'N	70° 12'E to 70° 18'E
2	Singharo Bhitro, Block-II	55.00	24° 44'N to 24° 51'N	70° 15'E to 70° 25'E

Source: Geological survey of Pakistan, Sindh Coal Authority

The Thar coalfield is located approximately between Latitudes 24°15'N and 25°45'N and Longitudes 69° 45'E and 70° 45'E in the southern part of Sindh Province in the Survey of Pakistan topo-sheet Nos. 40 L/2,5 and 6. Based on available infrastructure and favorable geology, the Geological Survey of Pakistan selected four blocks near Islamkot for exploration and assessment of coal resources. The blocks with names, area and coordinates are given in Table-5. The area is accessible by a 410-kilometre metalloid road from Karachi to Islamkot via Hyderabad-MirpurKhas-Naukot and Thatta-Badin-Mithi-Islamkot. A road network connecting all the major towns with Thar Coalfield has been developed. The rail links from Hyderabad is up to Naukot, which is about 100 kilometers from Islamkot.

Table 2 Research Blocks & Measurements

S/No.	Name/Blocks	Reserves M/T	Indicated	Inferred	Total
1	Sinhar Vikian Varvai, Block-I	620	1918	1028	3566
2	Singharo Bhitro, Block-II	640	944	-	1584

Source: Geological survey of Pakistan, Sindh Coal Authority

1.5 Statement of the Problem

Having large depth of coal treasure, Pakistan is still striving for other energy sources and facing crucial problems of energy. Research aim to address following questions in order to sort out the energy crises in Pakistan

1. Extent to which coal from thar coalfield can be utilized as energy sources for the fulfillment of the crises in Pakistan?
2. What is the ratio of Arsenic in Coal collected from Thar coal?
3. What is the combustion behavior of coal collected from the Thar Coal Field Pakistan?
4. Is the arsenic in coal of thar coal field Pakistan sufficient enough for the combustion of coal into energy source?

1.6 Hypothesis:

H₁₀ There is no significance proof of Arsenic presence in coals of Thar coal field of Pakistan

H₂₀ Arsenic Presence in Coals of Thar coalfield does not affect the combustion process of coal

1.7 Research Design

Study adopted the method of experimental lab based research designed on sample of coal acquired from Block 1 and Block 2 of thar coal field Pakistan. Study selected Agha Khan Lab for the experimental purposes, preliminary information is addresses in the paper from geological survey and secondary data from different sources. Initial In-charge Thar coal field Mr. Kaddafi Samejo was contacted for water analysis of Dig pit and initial Coal analysis from Block 1 and 2 of thar coal field.

Table 3 Water analysis of Thar Coal Field

Drill Hole	STP 3		STP 8	
	1	2	3	4
Sample No.	191.6-194.6	115.9-118.9	179.9 – 182.9	88.4 – 91.4
Interval tested m				
Conductivity	4500	4165	4550	5900
Chloride	2480	2610	2680	4020
Sulphate	.24	.28	.25	.48
Sodium	1306	1.348	1.395	2090
Potassium	30	32	33	41
Calcium	-	100	100	370
Iron soluble	.03	.04	.04	.40
Manganese	.44	.33	.25	.04

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Fluoride	1.9	1.53	1.49	1.29
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Source: Geological Survey of Pakistan

After acquiring water analysis report and coal samples from the block 1 and 2 from thar coal field, general properties of thar coal were need as the classification of thar coals (Samples) that we had, lab test from thar coal field generated the tabular results in table 8 for the classification of the thar coal.

Table 4 Composition of Sample Acquired from Block 1 and 2

Parameters	Sample Numbers							
	1	2	3	4	5	6	7	8
Proximate Composition (%)								
Moisture	41.19	37.62	42.09	48.10	45.80	48.80	46.38	45.98
Volatile matter	16.47	14.38	13.45	13.69	18.03	11.95	12.37	17.64
Ash yield	5.06	19.17	0.63	2.49	1.90	3.98	6.78	3.40
Fixed carbon	37.28	28.83	43.83	35.72	34.27	35.27	34.47	32.98
Ultimate Composition (%)								
Carbon ^b	27.49	21.28	17.88	29.16	32.03	26.85	25.41	29.88
Hydrogen ^b	6.06	7.49	5.01	5.45	5.65	5.52	5.73	5.76
Nitrogen ^b	2.22	2.95	1.91	1.99	1.88	2.13	2.21	1.93
Sulfur ^a	1.42	0.19	0.22	0.40	0.21	0.23	1.20	1.24
Oxygen ^c	58.17	48.27	74.39	60.26	58.58	60.81	56.94	56.96
Others								
GCV ^d (kcal/kg)	4289.4							
	6	3194.16	2541.36	3279.75	3850.16	2729.25	2980.58	2978.76
ASTM Rank				Lignite				

Study further focused on the extraction of sampled coal acquired from thar coal field block 1 and block 2 using the extraction scheme of BCR SES and BCR SS for the proof that coal contains the arsenic in thar. Further study also argues on the combustion process of the thar coal and its feasibility. The fresh coal samples (n=20) were collected from different seams of blocks I and II at depths ranging 120–200 m. 10 samples from each block were acquired for further investigation and apply extraction schemes on it. Sample were collected randomly from different ranges and transferred in polypropylene bags, on the field Sindh Thar Coal Authority assessed the process of sample collection. Coal sample were separated in laboratory on plastic tray and left for dry so that lab test and experiments could be applied on samples of coal. Total time taken for drying the coals took almost 10 days. Oven was used to dry out the coal samples and was prepared for grinding. 4 samples of coal from each block were separated and experimented for the arsenic presence and combustion behavior by converting Laboratory made ash (LMA).

1.8 Apparatuses Used.

Table 5 apparatuses used in the process

S/no	Apparatuses	Purpose	Lab.
1	mechanical shaker	mix, blend, or agitate substances in a tube or flask by shaking	Agha Khan Lab + Sindh Coal Authority Lab
2	centrifuge	used for the separation of fluids, gas or liquid, based on density	Agha Khan Lab + Sindh Coal Authority Lab
3	microwave oven	For the heating purpose	Sindh Coal Authority Lab
3	pH meter	to measure the acidity and alkalinity of a fluid	Sindh Coal Authority Lab
4	spectrophotometer	the amount of a known chemical substance, Arsenic (concentrations) is determined	Agha Khan Lab + LUMS
5	deuterium lamp	used for spectroscopy	Sindh Coal Authority Lab

III. Experiments and Results

Thesis presents the data generated in labs of thar coal and survey coal mining industry of Pakistan. The total As values in 40 representative coal samples collected from blocks I and II of Thar coalfield, ranged from 15.2 to 22.4 and from 17.4 to 19.3 mg/kg, respectively. The correlation of depths with As concentration in coal samples of block I were significantly higher ($r=0.67$; $p<0.05$) as compared to block 2 ($r=0.55$; $p>0.05$). One of

the major sources of As contamination of the environment is due to release from the combustion of As-containing coal (Finke man et al. 2002; Wang and Mulligan 2006). Therefore, the As contents in LMA were analyzed as shown in Table below:

Table 6 apparatuses used in the process

Block	ID	Depth (m)	Total As content	
			Coal	Ash
B-I	S1	70 –90	15.2–13.1	1.19–3.00
			16.15±0.16	1.60±0.19
	S2	112–132	17.1–11.9	0.79–3.26
			18.0±0.80	1.52±1.29
	S3	141-165	19.7–21.5	1.77–2.91
20.2±0.44			1.82±0.08	
S4	170-199	19.7–22.4	2.01–3.24	
		20.8±1.16	2.16±0.10	
B-2	S1	125–135	22.1–12.3	1.33–1.60
			22.2±0.02	2.47±0.19
	S2	160–165	17.4–14.6	2.14–2.96
			18.0±0.80	1.06±1.29
	S3	170–175	19.1–11.3	1.65–1.80
19.7±0.60			2.73±0.06	
S4	185–205	17.4–17.6	3.27–1.59	
		18.2±1.16	1.40±0.16	

Both methods are equally important and famously used in extracting coal process, for this study we have applied both the application procedures to extract the elements and understanding the presence of the arsenic in Block I and Block II than results are compared with each other. Following is the standardized formula to calculate the Arsenic presence:

$$\% \text{Recovery} = \frac{1}{4} \text{As extracted by propose BCR-SS}_{100}$$

$$\text{As extracted by propose BCR-SES}$$

For more perfect results and purified validation the method for accuracy, a certified reference material of sediment BCR 701 was also applied and analyzed. The resulted data obtained in 4 replicate samples of BCR 701 by BCR-SES and BCR-SS methods are summarized in Table 11. Both methods applies give same values of extraction shown in tabular format. The triplicate coal samples of each site of blocks I and II of Thar coalfield were subjected to BCR-SES and single extractions (BCR-SS) as shown in Table 12.

The comparison between BCR-SES and BCR-SS methods was calculated by paired t test and compared the t-experimental (t_{Exp}) to that of theoretical value ($t_{Critical}$ at 95 % confidence limit (Table 7). In cases of reducible and oxidizable fractions of As, the t_{Exp} was found to be 0.021 and 0.15, respectively, which are less than that of $t_{Critical}$ value (2.12), i.e., no significant difference was observed between the extractable As by BCR-SES and BCR-SS methods ($p > 0.05$).

Table 7 BCR results of LMA

BCR 701	Acid-soluble As	Reducible	Oxidizable	Residual	Σ Three steps residual	Pseudo-total As (%RSD)
		As	As	AS		
Indicative values						
BCR-SES	1.9	40.3	5.21	23.0	ND	97±0.21
BCR-SES	2.12±0.10	50.5±1.50	4.50±0.50	26.0±1.50	96.4±1.80	96.4±1.60 (4.10)
BCR-SS	2.12±0.15	55.3±2.60	5.24±0.50	–	–	– (4.80)
% Recovery	99	100	96	–	–	–
t Test values at df=5, $t_{Critical}=2.12$	–	0.021	0.15	–	–	–

A comparison between pseudo-total results of the BCR 701 sample, with those values obtained by BCR three steps + residual, indicates no significant difference (Table 12). The %recovery and relative errors (>97 and <1.0 %) indicated the validity of the proposed BCR-SS method (Table 7). Moreover, due to the

unavailability of a certified reference material of coal for As fractionation, the validity of the BCR-SES and BCR-SS extraction procedures were assessed using three replicate subsamples of coal collected from blocks I and II of the Thar coalfield, spiking with three known concentration levels of As standards. The percentage recovery of As in each fraction of BCR-SES and BCR-SS were >98 %, indicating no significant difference ($p>0.05$) (Table 8). The major benefit of proposed BCR-SS extraction procedure method is that all fractions can be extracted simultaneously, hence making it less time consuming as compared to the BCR-SES method. The limitation was that, greater sample amount required, as the solid residue was rejected at each step, however, it is not a problem where abundant environmental (soil, sediment, and coal) samples are available. The acid-soluble fraction is always directly extracted; so, for this step, results obtained by BCR-SES and BCR-SS were the same (Table 9), and our results are consistent with other studies (Margui et al. 2004; Mossop and Davidson 2003). The acid-soluble fraction of BCR 701 shows good agreement with indicative values of (As) as presented in Table 13 (Jamali et al. 2009; Sahuquillo et al. 2003). In the present work, it was observed that >9.0 % As was present as an easily extractable/acid-soluble fraction in coal samples of the Thar coalfield (blocks I and II), which could result in contamination of underground water due to variation in pH.

Table 8 results of thar coal standard coal

Table 13 The results of standard addition/recovery for As fractions in coal samples of Thar coalfield by BCR-SES and BCR-SS

ID	Added (mg/L)	Fraction 1		Fraction 2				Fraction 3			
		BCR-SES/BCR-SS	%R	BCR-SES	%R	BCR-SS	%R	BCR-SES	%R	BCR-SS	%R
B-I(S3 ^I)	0	1.92		2.67		2.83		11.54		11.90	
	1.5	2.38	96.3	3.14	97.3	3.30	97.3	12.95	97.3	11.35	97.3
	3	4.83	97.9	5.60	97.1	6.80	97.1	15.32	97.1	12.78	97.1
	6	09.82	98.2	11.58	97.1	9.75	97.1	21.34	97.1	21.73	97.1
B-II (S3 ^{II})	0	2.84		1.95		2.17		6.49		6.12	
	1.5	3.33	98.6	3.43	97.3	4.57	97.3	12.93	97.3	12.36	97.3
	3	5.83	98.8	5.93	97.6	7.15	97.6	11.41	97.6	14.09	97.6
	6	09.72	95.8	9.92	97.6	10.02	97.6	17.41	97.6	16.84	97.6

The sum of total extractable As contents (Σ three steps) obtained by BCR-SS were 1–2 % higher than those results obtained by BCR-SES in certified reference material (BCR and real coal samples (Tables 12, 13, and 14). The relative mobility of As in coal samples of the Thar coalfield blocks I and II were determined to be in increasing order: acid soluble < reducible < oxidizable fractions.

Three-stage sequential leaching test for As in LMA: The results of three-stage sequential extraction test for As in LMA of blocks I and II (because no thermal power plant is still in operational condition) is shown in Table 14. The resulted data obtained by three-stage sequential extraction for As in LMA is helpful to assess the concentration of As in different fractions of ash found after complete combustion. It has been observed that in water-soluble fraction of LMA, the As was found in the range of 0.05–1.01 mg/kg (Table 14), which corresponds to 4–18 % of total As in LMA. It represents the easily liable or readily exchangeable fraction of As in LMA/ completely combusted coal ash.

Table 9 Three-stage sequential extraction of As in ash samples of coal after burning

ID	Water-soluble fraction	Acid-soluble fraction	Residual fraction	Σ of three fractions	Pseudo-total As
s1 ^I	0.13–0.21	0.21–0.51	0.56–0.80	1.11–1.78	1.21–1.89
	0.19±0.02	0.22±0.03	0.45±0.06	1.23±0.05	1.23±0.15
s2 ^I	0.21–0.38	0.32–0.62	0.91–1.82	1.04–1.25	1.14–3.29
	0.29–0.01	0.21±0.04	1.23±0.23	1.12±0.03	2.54±0.98
S1 ^{II}	0.12–0.20	0.29–0.41	0.45–0.780	1.23–1.33	1.14–1.60
	0.16±0.01	0.30±0.01	0.56±0.03	1.21±0.02	1.43±0.19
S2 ^{II}	0.03–0.07	0.03–0.08	0.97–1.32	1.43–1.15	1.13–2.96

0.02–0.01 0.05±0.01 1.11±0.23 1.14±0.02 1.05±1.29

The fraction of As in LMA extracted by 0.1 M HCl is about 5–40 % of the total As content (Table 14). However, the residual fraction contained 30 to 90 % of As, which is considered to be present as primary or secondary minerals or silica oxide bounded As. The obtained resulted data are consistent with other studies. Gómez et al. (2007) stated that the volatility of As and other metals/ metalloids during coal combustion depends on their affinities, concentrations, physical changes, and chemical reaction with sulfur or other volatile elements.

IV. Conclusion

The proposed BCR-SS method shortens the lengthy treatment time required for conventional BCR sequential extraction procedure. However, both methods provided overall comparable information concerning the mobility and bioavailability of As under diverse environmental conditions. The proposed BCR- has been validated by standard addition method and certified reference material BCR 701 with %recovery >97 %. The extraction efficiency of As by BCR-SS was slightly higher than BCR-SES, ranged (100–104 %), while difference was not significant at 95 % confidence limit with <10 % precision. The total As in coal and LMA samples of block III were found to be high as compared to block V ($p < 0.05$). The relative higher mobility of As obtained in oxidizable fraction as compared to other fractions of BCR method in coal samples of blocks III and V indicated that major amount of As is organic bonded. The resulted data of three-stage sequential extraction for As LMA revealed that only 4–18 % of total As in LMA is easily liable, to create environmental risk. It was observed that the concentration of As in the reducible fraction of all studied coal samples was in the range of 14–16 % (Table 14). The low amount of reducible content of As in coal samples indicated that pyrite or Fe/Mn-containing minerals are present in trace quantity. The resulted data of oxidizable fraction indicates high level of As, because in coal, the large amount of organic matter is present. Moreover, the As concentrations extracted by BCR-SS procedure were considerably higher than those obtained using BCR-SES (Table 13). In present work, it was observed that 40–50 % of As is associated with the oxidizable fraction of coal, which is assumed to be consist of hydrocarbon and sulfide minerals.

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