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GEOCHEMISTRY OF ARSENIC AND ANTIMONY IN THAR COAL

Imdadullah Siddiqui

Centre of Pure and Applied Geology, University of Sindh Jamshoro

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Abstract

Thar coal is the largest coalfield of Pakistan, having 185 million tons of proven reserves. Thar coal have been analyzed for As and Sb and their environmental impact is assessed. Arsenic and antimony in coal belongs to iron sulphide association. The results show that in coal antimony (Sb) accumulates stronger than arsenic (As). Among all three blocks of Thar coalfield antimony ranges from 1.3 ppm to 3.2 ppm in Block-I; in Block-II, the concentration of Sb ranges from 1.3ppm to 3.7ppm; and in Block-III, it ranges from 1.4 ppm to 4.3 ppm. The concentration of arsenic in Block-I varies from 0.9 to 2.1ppm; in Block-II, it ranges from 0.8 to 2.7 ppm and in Block-III of Thar coalfield As ranges from 1.9 to 4.2 ppm.

In Thar coal, the probable source of arsenic and antimony is either hydrothermal solutions or the organic matter or pyrite present in coal.

Long-term exposure to antimony causes various health problems including respiratory effects. Exposure to arsenic may cause arsenicosis. It is therefore suggested that arsenic and antimony from Thar coal may be removed by sequential leaching process.

Keywords: X-ray fluorescent, arssenopyrite, hydrothermal fluids, arsenicosis.

1. Introduction

Thar desert is situated in a depression, bounded between the mountain belt of Hyderabad Arch to its west and the Indian shield towards its east (Jones, 1960). The Thar coalfield is located between latitudes 24°15'N & 25° 45' N and longitudes 69°45' E and 70° 45' E in the south eastern part of Sindh, on the stable western margin of the Indian Plate. It is connected with a 515 km metalled road upto Nagarparkar from Karachi.

The Thar coalfield is divided into following blocks:

1. Sinhar Vikian-varvai, (Block-I)
2. Singharo-Bhitro, (Block-II),
3. Saleh Jo Tar, (Block-III)
4. Sonalba, (Block-IV)
5. Saju Magho Bhil, (Block-V) and
6. Kharo Jani, (Block-VI)

However, drill core samples of coal were analyzed from first three blocks of Thar coalfield **(Fig. 1)**. Arsenic occurs as arsenopyrite in coal and a portion of the arsenic may occur as inorganic association in coal. In general, arsenic is associated with sulphide–rich fraction of the coal and most likely it is in the solid solution in the ferrous disulphide in coal, pyrite and marcasite (Karayigit *et al.,* 2000).

According to Gloskoter *et al.* (1977), Arsenic and Sb are strongly associated with the mineral matter fraction of the coal.

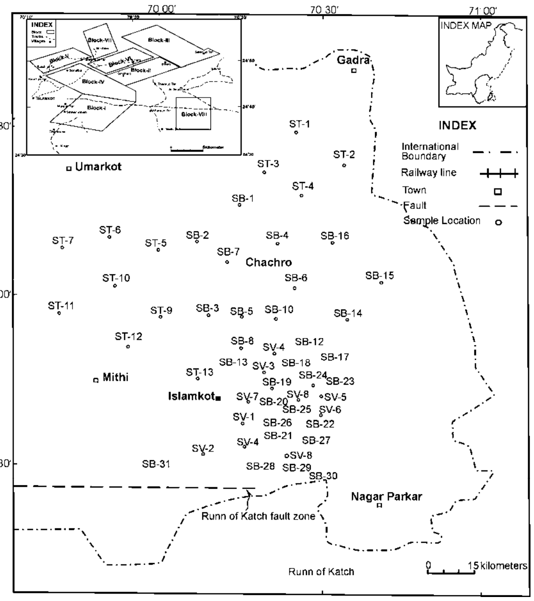


Fig. 1. Map showing location of samples collected from Thar coalfield.

Antimony may occur in both inorganic and organic forms. The most common of occurrence Sb is in pyrite and other sulfide minerals. Antimony is also found in clay minerals and organic matter in coal.

Antimony in coal may be present in solution in pyrite and as accessary sulphides e.g. stibnite ($Sb_2 S_3$) grains dispersed throughout the organic matrix (Finkelman *et al.,* 1990). The epigenetic stibnite is introduced after epigenetic quartz and calcite precipitated from hydrothermal fluids (Karayigit *et al.,* 2000). Sb in coal may be present in solution in pyrite and as minute accessary sulphides e.g. stibnite (Sb_2S_3) grains dispersed throughout the organic matrix (Finkelman and Palmer, 1997). The epigenetic stibnites were introduced after epigenetic quartz and calcite precipitated from hydrothermal fluids (Karayigit *et al.,* 2000).

2. Tectonics of the area

In the global tectonic perspective, Pakistan is situated at the junction of three lithospheric plates, the Indian, Arabian and Eurasian plates. The Indus Basin is situated on the north-western corner of the Indian Plate Fig. 2.

The Indian Plate started drifting in the northeastern direction during Jurassic to Early Cretaceous time and collided with the Eurasian Plate in Paleocene to Early Eocene. During Lower to Middle Cretaceous the Lower Indus Basin was subjected to extensional tectonics and block-faulting followed by volcanic activity, as witnessed in the southern Sindh in Pakistan and Kutch region in India **(Fig. 2)**.

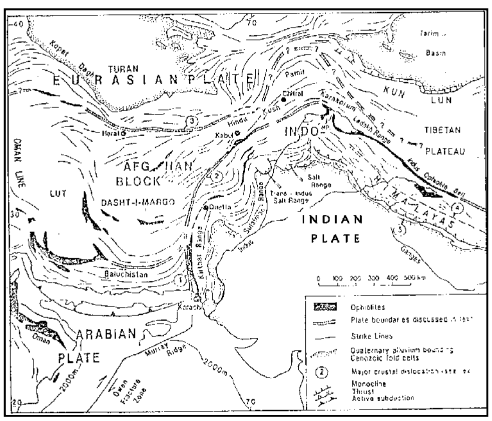
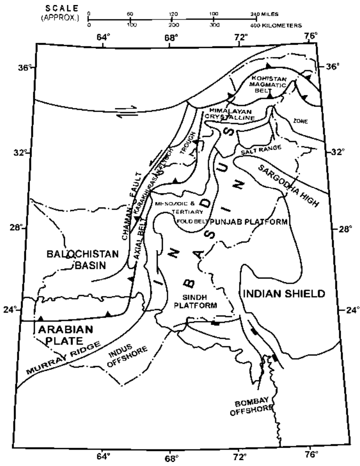


Fig.2. Map showing Pakistan and adjacent tectonic plate boundaries (after Bender and Raza, 1995).

Pakistan contains two sedimentary basins, the Indus Basin and the Baluchistan Basin. Thesebasins are separated by a major fracture zone, the axial belt; collectively occupy an area of about 828,000 sq. km (Fig. 3). The Indus Basin belongs to the class Extra Continental Down Warp Trough. The basin has elongated shape and is oriented in northeast-southwest direction. The main tectonic features of the Indus Basin are the platform, the foredeep comprising depressions, an inner folded zone and outer folded zone (Memon *et al.,* 1999) **(Fig. 3)**.

The Platform known as Indian Platform coincides with the present Indus Plain. Thar is part of the Indus Platform, this zone extends over an area exceeding 25,000 sq.km in the southeastern zone and



Fig,.3. Map showing tectonic divisions of Pakistan (after Raza *et al.,* 1989)

includes the Indus Plain and Thar-Cholistan Desert (Kazmi and Jan, 1997). In the eastern part Precambrian rocks form a gentle westward dipping monocline covered by a thin cover of Mesozoic to Cenozoic marine to deltaic sediments. Indus Platform is covered by unconsolidated Quaternary deposits with maximum thickness of about 500m. Precambrian Basement Complex was penetrated at varying depth between 110 to 277meters (Jaleel *et al.,* 2002). The basement rocks are represented by granite and granodiorite **(Fig. 4 and 5)**. The granite is of pinkish gray, to light

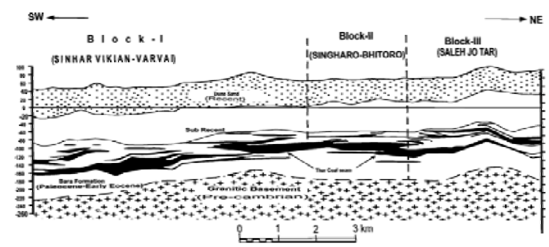


Fig. 4. Fig. showing generalized cross-section of Thar coalfield (Jalel *et al.,* 2002).

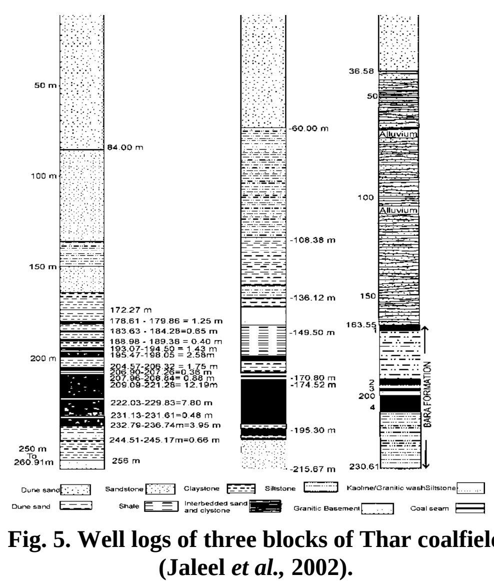


Fig. 5. Well logs of three blocks of Thar coalfield (Jaleel *et al.,* 2002).

gray in colour. A basic dyke of doleritic composition has been logged at various places (Jan *et al.*, 1997). Precambrian sequence is thinnest in the Tharparkar High (10-200m) and eastern margin of platform.

Table 1. The generalized stratigraphic sequence of the Thar coalfield (Jaleel *et al.*, 2002).

Formation	Age	Thickness	Lithology
Dune Sand	Recent	14m to 93m	Sand, Silt & Clay
……………. Unconformity ……………			
Alluvial Deposits,	Sub Recent	11m to 209m	Sandstone, Siltstone, Clay stone
……………. Unconformity………………			
Bara Formation	Paleocene to Early Eocene	+52m (variable)	Clay stone, shale, sandstone, coal, carbonaceous clay stone
……………Unconformity ………………			
Basement Complex	Pre-Cambrian	----	Granite and quartz ,diorite

3. Materials and Methods

Total fifty six core samples (13 from block-I, 31 from Block-II and 12 from Block-III) of Thar coal basin were obtained from core library of Geological Survey of Pakistan, Sindh regional office, Karachi. Figure 1 shows the location of the samples and analytical results are given in Table 2.

The X-ray fluorescent methods have been used for chemical analysis of elements in geological materials, including coal (Kiss, 1979; Kuhn *et al.*, 1980; Gluskoter *et al.*, 1977).

The basic principle of XRF is to bath the coal samples in the broad white radiation spectrum obtained from a standard laboratory X-ray tube. The absorption of the radiation by individual elements is generally by means of excitation of a 1s electron (K-edge) absorption process or a 2s or 2p electron (L-edge) absorption process for higher atomic number elements.

The collected core samples were of Thar coalfield, were grinded in a grinding mill up to the -200 mesh size. Ten grams of this powdered sample was taken and mixed with 1.24 grams of a wax that is used as a binder. Finally, 10 grams of this mixture were taken and pressed up to 25 N in a pressing machine to prepare a rounded pressed pellet. These pressed pellets were then put in a steel cup and transferred to the sampling chamber of Bruker-AX, S4-PIONEER machine. The elements are irradiated with 15-60Kv and 20-150mA current and analyzed by Geomajor Elements Software.

The sequential leaching procedure as described by Finkelman *et al.*, (1990) and Palmer *et al.*, (2004) was used during this study. Representative coal sample of studied coal feed was prepared by mixing of 50 grams, pulverized – 60 mesh of the Thar coal. solutions were then centrifuged and combined with different solutions and agitated for 18 Duplicate 100 gram samples of thes coal were hours separately. The solutions were then centrifuged and the leachates were separated by filtration. The samples were first leached with 1 N ammonium acetate ($NH_4C_2H_3O_2$). The procedure was repeated in subsequent leaching steps using 3N Hydrochloric acid (HCl), concentrated hydrofluoric acid (HF) and 2N nitric acid (HNO_3).

4. Results and Discussion

The analytical results of arsenic and antimony in Thar coal are shown in **(Table 2)**. Minerals and (Fig. 6). identified by X-ray Diffraction (XRD) analysis in Thar coal are shown in Table 2. Minerals identified by X-ray Diffraction (XRD) analysis shows that Thar coal are Quartz (SiO_2), kaolinite [($Al_2Si_2O_5(OH_4)$)], calcite ($CaCO_3$), dolomite ($CaMgCO_3$), muscovite $KAl_2(OH)_2$ ($AlSi_3O_{10}$)], illite [$KAl_2(OH)_2AlSi_3(O,OH)_{10}$] and pyrite ($FeS_2$) (Siddiqui *et al.*, 2009). Iron in analyzed coal is related to pyrite. Antimony (Sb) is primarily associated with mineral matter i.e. clay minerals.

The eight most common heavy metal pollutants listed by the Environmental Protection Agency (EPA) are As, Cd, Cr, Cu, Ni, Pb, Sb and Zn. Their toxicity varies with threshold limiting value (TLV=2 mg/m^3 to 500 mg/m^3) in air. From the environmental pollution point of view, the above metals may be broadly classified into the following categories:

(1) Non-toxic but accessible
(2) Toxic but non accessible
(3) Toxic and accessible

It is the third category of potentially toxic and relatively accessible metals that have attracted more attention due to their potential as environmental pollutant and posing threat to the public health. Nine trace elements (As, Cr, Mn, Ni, Pb, Sb, Se, Th and U), considered as potentially Hazardous Air Pollutants, and are present in low to moderate concentrations.

The concentration of As in the Thar coalfield varies from 0.9 ppm to 2.1 ppm (average 1.55 ppm) in Block–I, from 0.8 ppm to 2.7 ppm (average 1.59 ppm) in Block–II and 1.9 ppm to 4.2 ppm (average 2.91 ppm) in Block-III (Table 2). Table 2 and Fig. 6 shows that the Block-III of the Thar coalfield has relatively high As content.

Table 2. Arsenic (As) and Antimony (Sb) in ppm three blocks of Thar

Block (1 -I 3)			Block (3 -II1)			Block (1 -III 2)		
Sample No.	As (in ppm)	Sb (in ppm)	Sample No.	As (in ppm)	Sb (in ppm)	Sample No.	As (in ppm)	Sb (in ppm)
SV-1	1.7	1.3	SB-1	1.5	2.4	ST-1	2.4	2.4
SV-2	1.8	1.5	SB-2	1.2	3.2	ST-2	2.8	4.3
SV-3	1.4	2.3	SB-3	1.3	2.8	ST-3	1.9	2.8
SV-4	0.9	2.7	SB-4	2.2	1.8	ST-4	3.4	3.7
SV-5	1.2	1.5	SB-5	1.9	1.9	ST-5	2.2	1.4
SV-6	1.5	1.9	SB-6	1.7	1.7	ST-6	2.6	3.1
SV-7	2.1	3.2	SB-7	1.3	2.2	ST-7	3.8	2.7
SV-8	1.6	1.8	SB-8	2.1	2.5	ST-8	4.1	1.9
SV-9	1.9	1.9	SB-9	1.4	3.7	ST-9	2.4	4.3
SV-10	2.1	2.4	SB-10	1.7	1.8	ST-10	3.2	3.4
SV-11	1.3	1.6	SB-11	1.8	1.9	ST-11	4.2	4.1
SV-12	1	1.5	SB-12	1.5	3.2	ST-12	1.9	2.8
SV-13	1.6	1.9	SB-13	1.2	2.8			
			SB-14	1.6	1.9			
			SB-15	1.5	3.4			
			SB-16	2.3	1.3			
			SB-17	1.9	1.7			
			SB-18	1.5	1.9			
			SB-19	1.5	2.6			
			SB-20	1.2	1.8			
			SB-21	2.7	3.2			
			SB-22	1.8	1.8			
			SB-23	2.3	2.8			
			SB-24	1.1	1.9			
			SB-25	1.2	1.8			
			SB-26	1.4	3.4			
			SB-27	1.8	2.1			
			SB-28	1.0	1.9			
			SB-29	0.8	1.8			
			SB-30	1.2	1.6			
			SB-31	1.8	2.1			
Average	***1.55***	***1.96***	***Average***	***1.59***	***2.29***	***Average***	***2.91***	***3.08***

In **(Fig. 6, 7 and 8)** Fe, Ni and Co are plotted against As and Sb, but among these elements Fe vs As and Sb display a positive correlation, particularly in block-II (having R^2 value 0.1226), which could be considered as relatively better correlation.

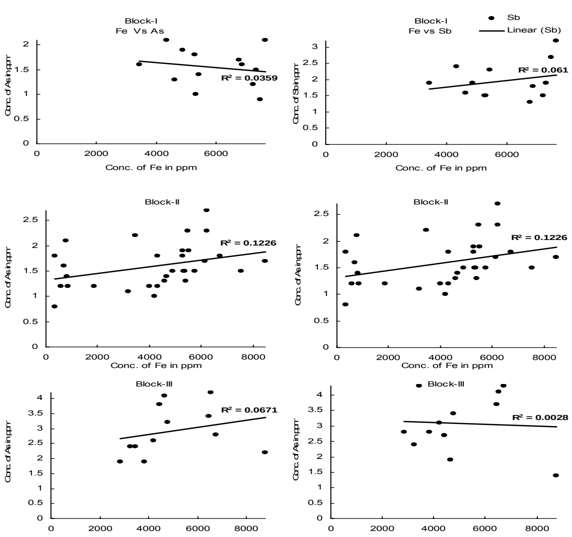


Fig. 6. comparison of Fe vs As and Sb in Thar coal.

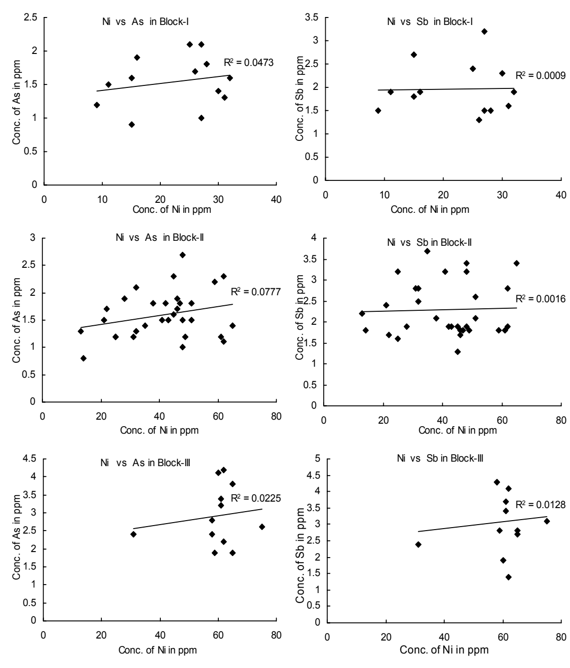


Fig. 7. Selected comparison of Ni vs As and Ni vs Sb in Thar coal.

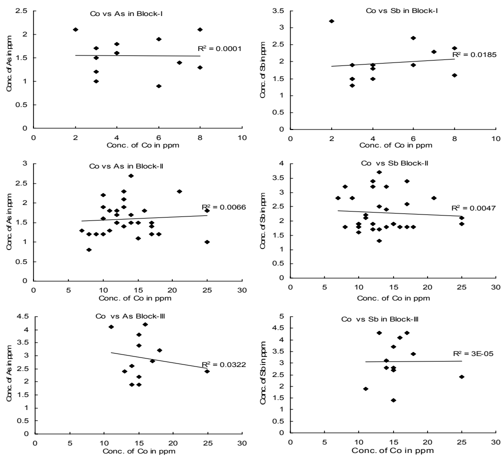


Fig. 8. comparison of Co vs As and Ni vs Sb in Thar coal

The average concentration of arsenic and antimony in Thar coal is compared with the coals from elsewhere in the world in Table 3. Arsenic concentration in U. S. lignite is 1.1 ppm, the Indian coal data is not reported. The Turkish coal has 2000 ppm, Chinese coal contains arsenic concentration of1100 ppm, Canadian coal contains 2527 ppm; and worldwide concentration of antimony is 3.0 ppm (Volkovi'c, 1983).

The concentration of Sb in the Thar coalfield varies from 1.3 ppm to 3.2 ppm (average 1.96 ppm) in Block – I, from 1.3 ppm to 3.7 ppm (average 2.29 ppm) in Block – II and 1.4 ppm to 4.3 ppm (average 3.08 ppm) in Block-III. Table 2 shows that Block-III is relatively high in Sb content.

As **(Table-3)** shows that antimony (Sb) concentration in U. S. lignite is 1.1 ppm (Volkovi'c, 1983), and worldwide concentration of antimony is 3.0 ppm (Volkovi'c, 1983).

Table 3. Comparison of various heavy and trace elements (in ppm)of Thar coal with the coals of various countries of the world.

Coalfiled/country	As	Sb
Thar coal	1.86	2.38
Indian coal[1]	N.R	N.R
Turkish coal[2]	2000	81
Chinese coal[3]	1100	2.2 µg/gm
Canadian coal[4]	3537	47.81
US coal[5]	1.1	1.1
Average worldwide coal[5]	3.0	3.0

NR = Not reported.
[1]Trivedy and Sinha (1990);
[2]Palmer *et al.* (2004);
[3]Zhang *et al.* (2004);
[4]Ripley *et al.* (1996);
[5]Valkovic′ (1983).

5. Conclusion and Recommendations

On the basis of experimental data, it shows that among the all three blocks, Block– III contain higher concentration (4.2 ppm; average 2.91 ppm) of arsenic and antimony (4.3 ppm; average 3.08 ppm). It is concluded that either the hydrothermal fluids precipitated from Kaolin/granite wash having quartz and clayey matrix, formed from the alteration of feldspar in quartz above the coal seams after coalification process. And antimony and arsenic is also believed that it might had enriched or leached out from the granitic basement granitic rock bellow the coalfield, and the fluids had transported As and Sb from Indian shield to the lignitic beds of Thar coalfield.

It is revealed that during combustion for power generation antimony and arsenic is released in atmosphere, and breathing high levels of antimony for a long time can irritate a person's eyes and lungs and can cause heart and lungs problems, stomach pain, diarrhoea, vomiting, and stomach ulcers. Ingesting large doses of antimony can cause vomiting.

Antimony (Sb) is potentially toxic element its adverse effects in coal are well known while high levels of arsenic exposure will cause arsenicosis, to the miners; it can cause nausea and vomiting, diarrhoea, anemia, and low blood pressure. These symptoms may be followed by a feeling of "pins and needles" in the hands and feet (neuropathy). Chronic (long-term) exposure to arsenic can cause stomach ailments, headaches, fatigue, neuropathy, dark splotches on the skin, and small "corns" or "warts" on the palms of the hands, to the coal miners (U. S. Environmental Protection Agency, 1999).

Based on the studies concerning the concentration of As and Sb in Thar coal it can be suggested that before the combustion in power plants, arsenic and antimony may be removed from Thar coal by the following processes:

1. Sequential leaching process provides a simple, direct method of determining the principal forms of occurrence of trace elements in coal. Elements that are leached by ammonium acetate in the first step are generally exchangeable. The next solution, HCl, dissolves those species, that are contained in acid-soluble oxides or carbonates such as $CaCO_3$. Elements present in silicate species, such as clays, are removed by HF solution. Sulphate compounds (including As and Sb or trace elements contained in pyrite) are removed by nitric acid.

2. The As from coal can be removed by benefaction and cleaning method.

3. Before the combustion, part of As escapes in gaseous phases and parts of As remain in fly ash and bottom ash. The As in bottom ash, when disposed off as solid waste may leach down and cause poisoning of underground water and soil.

It is therefore suggested that fin fabric electrostatic precipitators be used for collection and controlling As gaseous emission from power plants.

6. Acknowledgement

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