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X-RAY DIFFRACTION (XRD) ANALYSES OF THAR, SONDA AND METING-JHIMPIR COALFIELDS, SINDH

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Abstract

X-ray powder diffraction (XRD) is an instrumental technique used to identify unknown/various minerals. Rigaku X-ray diffractometer was used to record X-ray intensities scatters of the coal samples, collected from various coalfields of Sindh. Cu (K-alpha) radiations were used as X-ray source. These scatters shows that minerlogically the Sindh coals contain quartz and kaolinite as the dominant mineral phases with subordinate amount of calcite, dolomite, muscovite and illite. These minerals may have significance influence on the boiler of the power plant may also cause environmental degradation by producing emission of SO_2, CO_2.

Keywords: X-ray powder diffraction, sequential leaching of coal.

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1. Introduction

Coal is a complex combustible rock made up of organic and inorganic mineral components, each containing many elements. During combustion, elements present in the organic and mineral components of the coal are redistributed, as a result of high temperatures, into gaseous and solid phase reaction products such as coal combustible products (CCPs). Particle sizes, coal rank, amount of ash and coal mineralogy are controlling the combustion and mobility of elements in coal (Brownfield *et al*., 2005).

Four major coalfields named as (1) Sonda, (2) Meting-Jhimpir (both in Thatta district) (3) Lakhra (in Dadu district) and (4) Thar coalfield in Tharparkar are located in Sindh. The Sonhari coal is restricted to the Meting-Jhimpir coalfield, consisting of about 30m thick Sonhari Member, having sandstone and lateritic clay (Outerbridge *et al.*, 1991). The coal in Lakhra and Sonda coalfield was deposited in the Bara Formation, which is comformably overlain by the Lakhra Formation. The Bara Formation contains two main coal-bearing horizons; one is in the upper part and the other in the lower part. The lower one is known as Jheruck coal zone, found in Sonda coalfield. Sonda coal occurs relatively more persistently at three main horizons, named as Daduri, Sonda and Jherruck coal zone, and was deposited in the Bara Formation (Abbas and Atiq., 2005). Meting-Jhimpir coal is found in the Sonhari Member of the Laki Formation of Eocene age, near the contact with Upper Paleocene of Lakhra Formation (Wnuk *et al*., 1991).

Thar coalfield is the largest coalfield of Pakistan and is located on the Indus Platform in Thar Desert in south-eastern corner of Pakistan. It covers an area of about 9,000 sq. kms. It is located between latitudes 24°15'N and 25° 45' N and longitudes 69°45' E and 70° 45' E in the southeastern part of Sindh.

This coalfield is divided into following blocks **(Fig. 1 and 2).**

1. Sinhar Vikian-Varvai (Block-I) is southeast of Islamkot
2. Singharo-Bhitro (Block-II),
3. Saleh Jo Tar (Block-III) and
4. Sonalba (Block-IV) in the northeast of the area.

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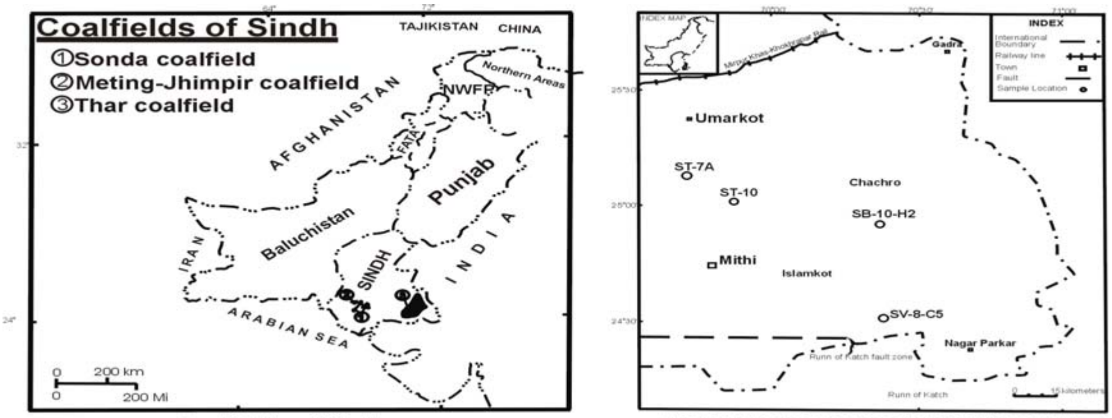
The maceral components indicate less maturity of coal formed from herbaceous plants in warm climate with rapid rise and fall in water level and environment of raised bogs (Fassett and Durrani., 1994). The quality of coal is lignite 'B'. Claystone forms the roof as well as floor rock of coal benches (Jaleel *et al*., 2002). Thar coals are Paleocene to Eocene in age and may have been deposited in a raised bog environment (Jaleel *et al*., 2002).

These studies show that coal bearing strata of Palaeocene–Eocene sediments unconformably overlie the Pre-Cambrian basement rocks of igneous origin which are exposed at Nagar Parkar and form the only outcrop in the area.

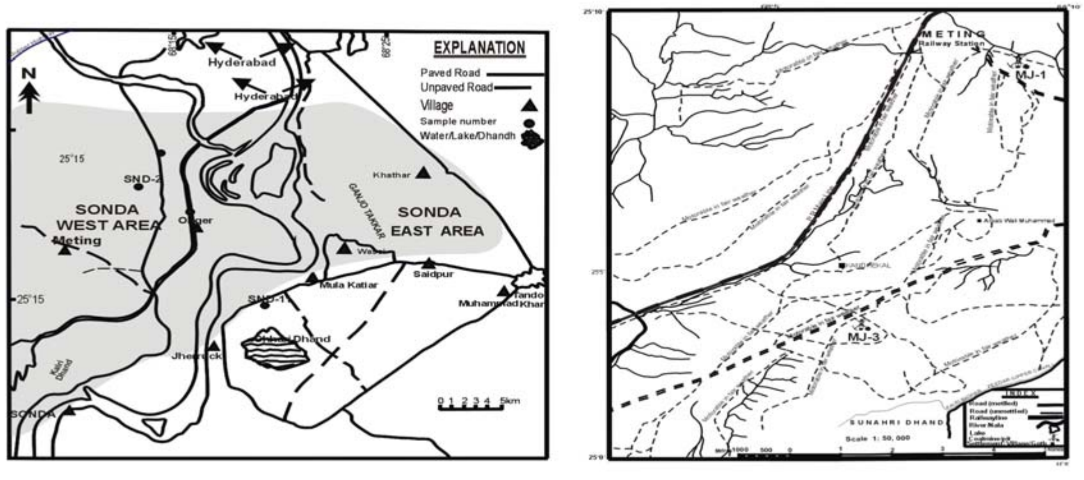
The basement rock is generally granitic in composition, which is highly altered to kaolinite. The Paleocene-Eocene coal bearing horizons, known as Bara Formation generally comprises of claystone, carbonaceous claystone, sandstone, and siltstone with inter-laminated coal beds. Sandstone is very fine-to coarse-grained and consists dominantly of quartz and minor amounts of ferromagnesian mineral grains. The lower 15-20 metres of the formation that consists the coal is saturated with brackish water (Khan *et al*., 2002).

The chemical analysis of the samples is summarized in **Table-1** (Siddiqui, 2008). The concentration of the Calorific value varies from 9835 btu/lb (in Meting-Jhimpir coal) to 11418 btu/lb (in Thar coal), while the ash content is in the range of 4.76% (in Sonda coal) to 11.56 % (in Meting-Jhimpir coal), Fixed Carbon ranges from 39.34% (in Meting-Jhimpir coal) to 45.34% (in Thar coal). The rank of Thar coal is lignite 'B', Sonda coal is ranked as lignite-A to bituminous-C and Meting-Jhimpir is bituminous coal (Siddiqui, 2008).



Coalfields of Sindh

Map showing locations of samples collected from Thar coalfield.



Map showing sampling location in Sonda coalfield.

Map showing location of samples in Meting-Jhimpir coalfield.

Figure 1. Maps showing locations of samples collected from Thar, Sonda and Meting-Jhimpir coalfields.

Table-1. Proximate, Ultimate (in percent) and Calorific value (in Btu/lb) analyses of Sindh

Sample No.	Thar Coal				Sonda Coal		Meting-Jhimpir coal	
	SV-8-C5	**SB 10-H2**	**ST-7A**	**ST-10**	**SND-2**	**SND-11**	**MJ-1**	**MJ-3**
Fixed Carbon	39.45	45.34	45.67	40.03	41.34	42.17	39.34	40.23
Ash	4.89	5.87	5.67	5.56	5.23	4.76	11.56	11.23
Hydrogen	6.01	7.22	6.97	6.97	6.34	5.85	6.89	7.12
Carbon	61.54	64.23	63.45	63.45	64.12	58.34	62.78	56.78
Nitrogen	0.30	0.36	0.35	0.35	0.32	0.29	0.36	0.24
Sulphur	1.89	1.05	0.44	0.44	3.80	6.50	2.96	3.12
Calorific Value	9863	11335	11418	11418	10335	10543	9835	10058

2. Material and methods

The coal samples collected from the coalfields of Thar, Sonda and Meting-Jhimpir (Fig. 2), and pulverized or grounded with mortar and pestle and prepared as per method described by Klug and Alexander (1974). The X-ray difractometer (XRD) analyses of selected coal samples were carried out on the Rigaku XRD, with Cu (K-alpha) as a source of X-rays and the radiations generated at a tube voltage of 40Kv and tube current of 25mA. The X-ray Diffraction patterns of the 2θ verses intensity for an angular range of 2-37^{o} were obtained. The Joint Committee on Powder Diffraction Standard Mineral Powder Diffraction Files (1980) were used for interpreting the diffractograms by the Hanawalt methods of qualitative analysis. The XRD peaks/patterns of the Thar, Sonda and the Meting-Jhimpir coal are shown in **(Fig. 3 and Table 2) (a and b).**

3. Description and Discussion

The mineralogy of the selected whole-coal samples of Thar, Sonda and Meting-Jhimpir coalfields as interpreted by XRD patterns shows that the majority of the Thar coal contain quartz (SiO_2), kaolinite ($Al_2Si_2O_5(OH_4)$ as the dominant mineral phases while calcite ($CaCO_3$), dolomite ($CaMgCO_3$), muscovite [$KAl_2(OH)_2(AlSi_3O_{10})$], illite [$KAl_2(OH)_2AlSi_3(O,OH)_{10}$] are also present in lesser amount. The XRD patterns of the Sonda coals (Fig. 2) and the Meting-Jhimpir coals (Fig. 2) suggest that the quartz and kaolinite are the dominant while calcite, dolomite and pyrite are the subordinate mineral phases in both type of coals.

The mineralogy of the Sindh coalfields suggests that there seems to be two mineral suites in the Sindh coals:

1. Primary detrital suite, the primary detrital suite consisted of quartz and muscovite, and

2. An authigenic suite, authigenic mineral suite consisted of kaolinite, calcite, dolomite and illite.

The detrital minerals (i.e. quartz and muscovite) may have been derived from the basement rocks (granite) that have very high quartz and minor muscovite contents. There could also be some input from the plant-derived silica in the marine environment or the quartz overgrowth on the beta-form of quartz grains. Kaolinite may have been present as plant-cell fillings. The carbonates (calcite and dolomite) occur within coal marcerals and are usually associated with clay minerals and appear to be as diagenetic (syngenetic) minerals and may be present as secondary phase probably formed as a result of sulphur reduction of marine environment.

This suggest that the studied coals may cause sever problems in mining of these coals because of oxidation and formation of soluble toxic organic compounds of heavy and trace elements and hence contamination of underground water.

Table-2 (a). Peak position and d- spacing values of the minerals on the XRD Diffractogram identified in Thar coal samples

Sample No.	**Peak position** in degrees (2θ) angle	Mineral	***d-spacing*** (A°)
(a) SV-8-C5	12.6	Kaolinite (K)	7.02
	20.9	Quartz (Q)	4.25
	26.75	Quartz (Q)	3.33
	29.15	Calcite (C)	3.06
(b) SB-10-H2	12.5	Kaolinite(K)	7.08
	14.25	Illite (Ill)	6.21
	20.1	Illite (Ill)	4.41
	23.25	Calcite(C)	3.82
	25.05	Kaolinite(K)	3.55
	27	Quartz (Q)	3.30
	31.25	Dolomite (D)	2.86
(c) ST-10	10.75	Kaolinite (K)	8.22
	20.85	Quartz (Q)	4.26
	24.95	Kaolinite (K)	3.57
	26.8	Quartz (Q)	3.32
ST-7A	12.2	Kaolinite (K)	7.25
	20	Illite (Ill)	4.44
	25	Kaolinite (K)	3.56
	26.7	Quartz (Q)	3.34
	29.75	Calcite (C)	3.00

Table - 2 (b). Peak position and *d*-values of the minerals on the XRD Diffractogram, identified in Sonda and Meting-Jhimpir coal.

Sonda coal				Meting-Jhimpir coal			
Sample No.	**Peak position** in degrees (2θ) angle	Mineral	***d-spacing*** (A°)	Sample No.	**Peak position** in degrees (2θ) angle	Mineral	***d-spacing*** (A°)
SND-2	26.75	Quartz (Q)	3.33	MJ-1	24.45	Calcite (C)	3.64
	31.25	Dolomite (D)	2.86		29.4	Calcite (C)	3.04
					31.35	Dolomite (D)	2.85
SND-11	29.5	Calcite (C)	3.03	MJ-3	21	Quartz (Q)	4.23
	31.25	Dolomite (D)	2.86		26.9	Quartz (Q)	3.31
					29.35	Calcite (C)	3.04

The mineral matter in coal will affect the boiler of power plant, when the of mineral groups, like clays, quartz, sulphides and carbonates are decomposed. The XRD analyses of coal from Thar, Sonda and Meting-Jhimpir shows the presence of Quartz and clay minerals (kaolinite and illite). Kaolinite has a chemical composition that varies little from the formula $Al_2S_{i2}O_5(OH)_4$., while the illites have a wide range of chemical compositions based on muscovite [$KAl_3S_iO_{10}(OH)_2$]. During combustion this clay melts in boiler and gives an aluminosilicate liquid that usually contains small crystals of mullite [$A_{l6}S_{i2}O_{13}$]. In this way pure kaolinite melts more slowly than the other clay minerals.

In the same way quartz has a composition that differs little from that of pure S_iO_2. Quartz grains melt more slowly than other minerals. During combustion, pyrite readily loses sulphur to form pyrrohtite [FeS_{1-x}] which then oxidises, passing through a molten iron oxy-sulphide stage before forming magnetite [Fe_3O_4]or hematite [Fe_2O_3],(Groves *etal.* (1987).

The dominant carbonate mineral in Sonda and Meting-Jhimpir coal are calcite [$CaCO_3$], and dolomite [$CaMg(CO_3)_2$]. Calcite may fragment as it heats up rapidly.

4. Environmental impact of minerals in coal

During the combustion of minerals in coal may transform in response to the high temperatures, in this way clay minerals and quartz fully or partially fuse to form a viscous melt. Pyrite loses sulphur and oxidises through a liquid Fe-S-O stage to solid iron oxide. This mineral is hard and very abrasive; it decomposes and fuses at a relatively low temperature, and also emits sulphur-containing gases when the coal is burned. In Sonda and Meting-Jhimpir coal, the dominant carbonate mineral calcite [$CaCO_3$], and dolomite [$CaMg(CO_3)_2$]; will emit CO_2 and will deposit solid oxide products. Mineral occurrences that contain two intimately associated minerals, calcium, from calcite, may interact with transforming clay minerals to produce calcium-rich aluminosilicate ash particles.

5. Demineralization of Sindh coal

The sequential leaching procedure as described by Finkelman *et al*., (1990) and Palmer *et al*., (2000) was used during this study. One representative coal sample of Sindh coal feed was prepared by mixing of 50 grams, pulverized – 60 mesh, each of the Thar coal, Sonda coal and Meting –Jhimpir coal. Duplicate 100 gram samples of this coal were combined with different solutions and agitated for 18 hours separately. The solutions were then centrifuged and the leachates were separated by filtration. The samples were first leached with in 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).

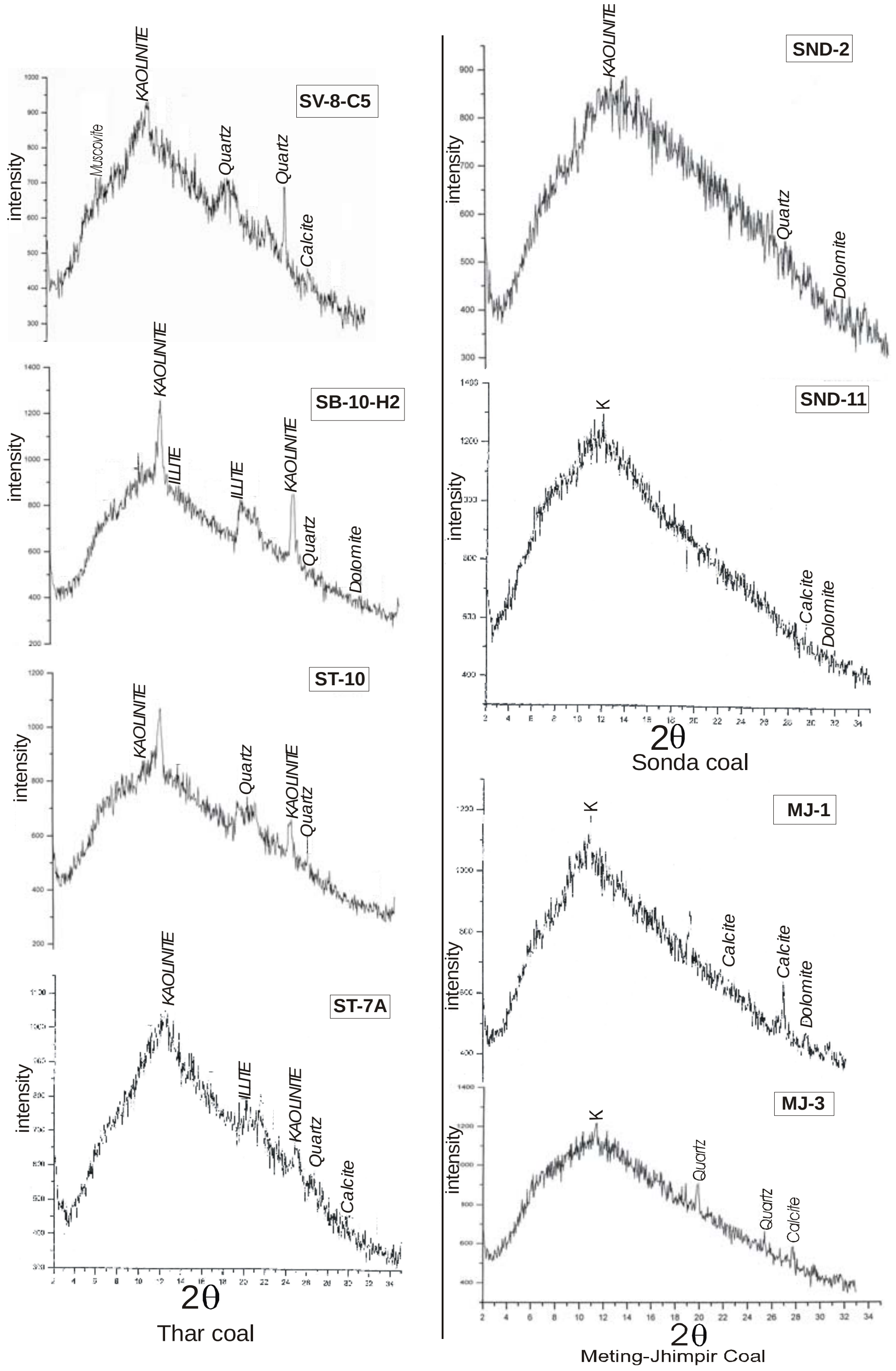
Sequential leaching techniques are used to develop models for the demineralization of Sindh coal and to predict the behavior of the potential leaching of coal combustion products (Brownfield, 2005). The sequential leaching analysis were performed on the Sindh coal and the chemical data were processed to obtain the percentage for each elements leached by four solvents.

In this experiment sequence of solvent was selected, so that (1) exchangeable cations, water soluble compounds and some carbonates are removed by $NH_4C_2H_3O_2$; (2) cations associated with carbonates, mono-sulfides, iron oxides and chelated organic compounds can be removed by HCl; (3) elements associated with silicates can be removed by HF and (4) elements associates with disulfides, especially pyrite and marcasite, would be removed by using HNO_3 (Brownfield, 2005). The sample residue present following the sequential leaching procedure contains the insoluble elements associated with the organic matter and the insoluble or shield minerals (Brownfield, 2005). It is clear that 40 percent or more are associated with HCl-soluble compounds such as carbonates, mono-sulfides, oxides, phosphate and sulfates where as more than 30 percent are associated with insoluble phases or organic shielded matter. 60 percent of pyrite (when oxidized as molten iron oxy-sulphide during combustion) is associated with HNO_3 soluble compounds while some portions (5-15%) of all the elements are associated with HF and HNO_3 soluble compounds including clays and silicates and pyrite and disulfides. This suggests that minerals in coal mainly occur as mono-sulfides or oxides and carbonates, whereas Co and Mn generally occur as oxides. Pyrite and marcasite are mainly occurring in the form of disulfides. Shielded matters generally occur as insoluble organic matter.

6. Conclusion

The mineralogy of the Sindh coals suggests that these coals have quartz and kaolinite as the dominant phases with minor amount of calcite, dolomite, illite and muscovite. The dominant minerals of Thar coal are quartz, that is harder than steel, these minerals

Fig. 2. X-ray Diffractogram showing the peak position of minerals in coal samples from Thar, Sonda and meting-Jhimpir coalfids of Sindh, Pakistan.



cause wear and abrasion in the boiler of power plant. Quartz is particularly hard and shatters to produce sharp-edged fragments. Quartz also tends to occur in the form of comparatively large particles of ‘free’ mineral matter, whereas much of the pyrite is dispersed in the coal substance and clay sediment. Other minerals such as the clays, carbonates and sulphates minerals are relatively soft and do not cause any significant erosion wear. For the removal of minerals from Sindh coal, washing or sequential leaching technique should be used by leaching coal in $NH_4C_2H_3O_2$, HCl, HF and HNO_3 acids.

Non-silicate minerals, found in studied coal, can have a significant influence on the boiler of plant. These will cause emission of sulphur during combustion, carbonate bearing Sonda and Meting-Jhimpir coal will also cause emition of CO_2.

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