

Coal Chemistry and Morphology of Thar Reserves, Pakistan

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ABSTRACT

The surface of Thar coal has been characterized by spectroscopic, microscopic and chemical methods using atomic absorption spectroscopy, fourier transform infrared analysis, X-ray diffraction, scanned electron microscopy and pH titration. The samples contained high moisture, low volatile and low to moderate sulfur content and ranked as lignite (heating value 2541 - 4289 kcal/kg on moist, mineral-matter-free basis). Scanned electron micrographs show porous matrix with calcium, potassium or sodium minerals. Fourier transform infrared analysis also confirmed the presence of aluminum, silica and hydrate mineral constituents. The spectra showed C=C aromatic groups at 1604 - 1609 cm⁻¹. Phenolic ester and carboxylic acid are identified by C=O stretching vibration peaks at 1702 cm⁻¹. The peaks of quartz and kaolinite were observed at 900 - 1100 cm⁻¹. Point of zero charge of Thar coal has been estimated as 6.00 to 6.27 through adsorption of H⁺ and OH⁻ ions by suspending coal particles in aqueous electrolyte solution. Oxygen containing functional groups, mineral matter, and metal oxides are found to have a remarkable impact on point of zero charge. The surface characterization study will be helpful in the separation of hydrophilic impurities during coal preparation processes considering pzc as the controlling factor.

Keywords: Coal Chemistry; Lignite; Surface Characterization; Scanned Electron Microscopy; Fourier Transform Infrared Analysis; X-Ray Diffraction Analysis; Point of Zero Charge

1. Introduction

Run-of-mine coal consists of coal, minerals and contaminants of large particle size. It needs a series of coal preparation steps after pulverization. During mining, crushing and other mechanical operations a significant amount of coal fines (particle size < 0.5 - 0.6 mm) is produced. The handling of fine particles is difficult, expensive and needs special attention [1]. There are several physical methods for the separation of minerals and other impurities from coal [2,3]. Physical cleaning through gravity separation has been recommended for lumps of coal but it is considered inefficient for fine particles [4]. Of the existing fine coal cleaning techniques, froth flotation method is the most common and effective. The process consists of bubbling air through coal/water slurry. The separation occurs by preferential physical attachment of air bubbles to the coal. The coal particles floated at the surface are removed, while the unwanted particles completely wetted and stay in the water phase. The ability of air bubbles to selectively adhere to coal is concerned

with the surface chemistry. Therefore, surface characterization of coal plays a vital role in coal preparation processes (such as floatation, dispersion, wettability, and coal-water slurry) prior to its utilization.

Generally fourier transform infrared (FT-IR) analysis, X-ray diffraction (XRD), and scanned electron microscopy (SEM) techniques are used for surface characterization of coal and coal-derived products [5,6]. Various industrial operations depend on the pH where electrical charge density on coal surface becomes zero (pzc); but limited data is reported in which pzc of coal has been considered as an important surface parameter [7,8]. When coal is immersed in a liquid environment, a charge is developed on its surface by dissociation of functional groups or by the adsorption of H^+ or OH^- ions [9]. The surface charge together with counter ions constitutes the electrical double layer and responsible to control the stability of coal suspensions (Figure 1). During adsorption phenomenon, if the pH is equal to pzc, the surface of coal acts as neutral specie. Below pzc, the surface of adsorbent becomes positively charged and attracts anions. Conversely, above pzc the surface becomes negatively

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Figure 1. Schematic representation showing role of pH on surface dependent processes of coal.

charged and attracts cations. Therefore, the charge on the surface of coal plays a significant role in the removal of unwanted species.

Thar coalfield has been recently discovered in Tharparker District of Sindh Province. It is the largest coalfield of the country (covering an area of 9100 km²) with estimated reserves of about 175.5 billion tones. Unfortunately the huge reserves are not exploited yet. However, now serious efforts are going on at government level to utilize these reserves. Our present understanding about the nature of Thar coal is surprisingly limited, which restricted from its efficient utilization [10]. The main objective of this study is surface characterization of Thar coal. Direct examination of surface of Thar coal by SEM, FT-IR, and XRD has been performed to obtain some useful qualitative information related to morphology, functional groups and mineral matters identification. These information are useful in the utilization of the reserve for various applications. SEM describes the suitability of coal surface for gasification process because diffusion of gases is easily permitted from porous surface. FT-IR analysis is helpful for the determination of functional groups which are the most reactive components in conversion processes. XRD tells about the mineral constituents of coal which are converted into ash during combustion. Mineral composition determines the mode of ash removal. An important outcome of the present study is surface quantification by measuring pzc. With the help of this important parameter one can identify the pH where the coal surface behaves as the least stable state. It is a major controlling factor in the separation of oxides, silicates, etc. Proper choice of pH is a requirement for selective flotation of one mineral from another.

2. Experimental

Eight samples of coal were obtained from Thar coalfield of Pakistan. The samples were air dried (ASTM D-3302-00a) and ground into fine powder of particle size 60 mesh (ASTM D2013-00a). Thermogravimetric analyzer (TGA-2000 A, Las Navas Instruments) was used to measure proximate analysis of coal according to ASTM D7582. Isoperibol bomb calorimeter (Parr 6300, USA) was used to measure the heating value in accordance with ASTM D5865-00. The elemental composition of the samples (C, H and N) was calculated using empirical formula derived by Carpenter and Diederichs [11]. Total sulfur was estimated using SC-32 LECO sulfur determinator (ASTM D 4239-00). The percentage of oxygen was taken by difference. Each analysis was performed in three replicates to check the reproducibility. Experimental data was converted into different basis using ASTM D388-99.

Fourier Transform Infrared (FT-IR) spectra of coal samples were recorded using NicoletTM 380, Fourier Transform Infrared Spectrophotometer (Thermo Electron Corporation, USA), with spectral resolution of 4 cm⁻¹. Major and minor oxides in the combustion residue of coal were analyzed by Perkin Elmer-2380 model atomic absorption spectrophotometer (ASTM D-3286). National Bureau Standards 1633a and 1635, Washington DC

were used as the standard reference materials. Mineralogical characterization was performed by X-ray diffraction using monochromatic Cu K \propto radiation at 40 kV and 30 mA ($\lambda = 1.5406$ Å). Microscopic observations were made using a JEOL JSM-6380A type scanning electron microscope at the accelerating voltage of 10 - 15 kV.

The surface charge at coal/water interface was determined by pH titration [12]. Two experiments were conducted for the purpose, each with 10 g of coal suspended in 35 ml of 0.1 M NaNO₃. After waiting 15 min to attain the equilibrium, one suspension was titrated with 0.1 M HNO₃ and the other with 0.1 M NaOH. The surface charge q_H and q_{OH} for HCl and NaOH additions respectively was estimated using Equations (1) and (2).

$$q_{\rm H} = \frac{C_{\rm a} - \left[{\rm H}^+ \right]}{m} \tag{1}$$

$$q_{OH} = \frac{\left[OH^{-}\right] - C_{b}}{m}$$
(2)

where C_a and C_b are the concentration (mol·L⁻¹) of added acid and base, respectively, H⁺ and OH⁻ are the molar proton and hydroxide ion concentration, and *m* is the mass of solid in g. The surface charge as a function of pH is calculated and plotted using Equations (1) and (2). The pzc was estimated as the pH where the surface charge crosses the x-axis (q = 0).

3. Results and Discussion

Physico-chemical properties of coal samples are shown in **Table 1**. The quality of coal was assessed on *as-received* basis [13].

Table 1. Classification of Thar coal samples (basis are shown in superscript).

Dovemeters				Samp	le No:			
raraineters	1	2	3	4	5	6	7	8
Proximate Composition ^a (%)								
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)	4289.46	3194.16	2541.36	3279.75	3850.16	2729.25	2980.58	2978.76
ASTM Rank				Lig	nite			

^aar basis = as-received basis; ^bdaf basis = dry, ash-free basis; ^cdb basis = dry basis; ³m, mmf basis = moist, mineral-matter-free basis.

The samples show high moisture, low volatile matter and low ash content (except sample 2 of high ash). High moisture content is attributed to the water aquifers which are present at Thar at an average depth of 50 m, 120 m and more than 200 m. The sulfur content in the samples is low to moderate. Ultimate analysis shows total carbon 17.88% - 32.03%, hydrogen 5.01% - 7.49%, nitrogen 1.88% - 2.95% and oxygen 48.27% - 74.39% on *dry-ashfree* (*daf*) basis. The samples are classified as lignite on the basis of gross calorific value (GCV) on *moist, mineralmatter-free* basis (ASTM D388-99).

3.1. SEM Micrographs

SEM images of Thar samples are shown in Figure 2 (a to h). The samples show interconnected and open micropores (<4 - 12 Å), mesopores (12 - 300 Å), and macropores (>300 Å) [14]. The SEM micrograph shows that coal matrix is covered with bright and dark luminous materials indicating the presence of minerals. The bright glow is due to the presence of calcium, aluminum, potassium or sodium. The dark luminosity is mainly due to the presence of chalcophiles [15]. The minerals are in the form of irregular shaped aggregates. Non luminous portion on the surface is mainly made up of carbon content. Randomly distributed fissures, cracks and etched pits could also be seen on the micrograph. These might be produced from the calcinations of dolomite and calcites as a result of thermal shock during metamorphism [16]. It is evident from the images that Thar coal contains large proportions of silica, calcium carbonates and dolomite, as well as some proportions of elements such as aluminum, potassium and sulfur.

3.2. FT-IR Analysis

Figure 3 shows FT-IR spectra of the samples. It is evident that Thar coal contains aliphatic CH, CH₂, and CH₃ groups, as well as aromatic ring systems. It also contains C-O-, C-O-C and associated -OH or NH bonds, and few C=O bonds. The band at 3350 - 3385 cm^{-1} is assigned to associated OH and NH groups (hydrogen bonded). All samples exhibit band at 2916 cm⁻¹ with a shoulder peak at 2850 cm⁻¹ showing the presence of aliphatic C-H stretching vibration. The strong band at 1604 - 1609 cm⁻¹ is attributed to aromatic ring vibrations, enhanced by oxygen groups [14]. The shoulder peak at 1702 cm⁻¹ (C=O stretching vibration) is represented phenolic ester and carboxylic acid [15,16]. All samples of Thar show lower intensity of the aliphatic methylene band at 1460 cm⁻¹ as compared to the methyl band at 1370 cm⁻¹ indicates that coal is composed of fewer aliphatic methylene groups than methyl groups [14]. Weak bands at 1560 cm⁻¹ was identified showing condensed aromatic ring C=C at their surfaces. The prominent peak at 1030 - 1035

cm⁻¹ with a shoulder peak at 1005 - 1010 cm⁻¹ is represented to Si-O bending vibration. Quartz and kaolinite were identified by the presence of bands in the region of 912 - 917 cm⁻¹ [5]. The aromatic character of coal due to C=C stretching vibration is found to be more pronounced than the aliphatic character as the band intensity at 1620 cm⁻¹ is higher than the bands at 2960 cm⁻¹ (stretching vibration of methyl's group). The same finding has been observed in FT-IR spectrum of Pittsburgh No. 8 coal [5].

3.3. Point of Zero Charge (pzc) Determination

The surface of coal is generally considered as negatively charged due to the presence of polar functionalities, dominantly carboxylic and phenolic groups. pzc of coal depends on the relative affinity of the coal surface for H⁺ and OH⁻. **Figure 4** describes that Thar coal behave at the least stable state at pH 6.00 - 6.27. At this pH range noncharged coal particles are supposed to be unable to bond with water. The maximum hydrophobicity of coal at this pH range supports the maximum floatability [17, 18]. pzc of Thar coal is attributed to the presence of weakly acidic oxygen groups, and ash forming minerals such as kaolinite and quartz etc. pzc of pure carbon is 6.5 - 7.0 while pzc of silicate minerals is approximately 2.0.

The presence of silicate minerals has been confirmed by X-ray diffraction analysis (**Figure 5**). pzc of Thar coal also depends on the minor oxides present in significant amount in the inorganic part of coal such as Fe_2O_3 (pzc 8.5) and CaO (pzc 8.1) [19]. The pzc of Thar coal will be of great importance for process engineers to control wet washing processes which depends on stability and coagulation of colloidal dispersion.

3.4. XRD Analysis

A typical XRD spectrum of Thar coal has been shown in **Figure 5**. The samples were composed of hexagonal shaped quartz low, dauphine-twinned SiO₂, monoclinic carbon oxide hydrate (COOH)₂·2H₂O and triclinic Kaolinite 1 A Al₂(Si₂O₅)(OH)₄. The mineralogical analysis was supplemented with the metal oxide quantification by atomic absorption spectrophotometer (**Table 2**). Higher amounts of SiO₂ and Al₂O₃ verified XRD observations.

3.5. Comparison of Thar Coal with Other Lignite Coalfields

In addition to characterization of the samples, chemical composition of Thar coal was compared with other lignite coals of the world. The samples of Thar are seems to closely resembles with the lignite coal mines of North Dakota with ultimate composition (C 30.46% - 34.25%, H 6.49% - 7.12% and N 0.50% - 0.56%) and oxide composition of



Figure 2. SEM images of Thar coal: (a) to (h) represents sample 1 to 8 respectively.



Figure 4. Point of zero charge of Thar samples, Sample No: 1(○), 2 (□), 3 (-), 4(×), 5 (●), 6(*), 7 (△), 8 (♦).



□01-080-0885(C)-Kaolinite 1a-A12(Si2O5)(OH)4 -Y: 65.50% -d x by: 1. -WL: 1.5406 -Triclinic -a 5.15550 - b 8.94380 -c 7.40510 -alpha 91.700 -beta 104.840 -gamma 89.830 -Base-centered -C1(0) -2-329.909- | / |

Figure 5.	A t	vpical	XRD	spectrum	of	Thar	coal.
		.,					

	Sample No:								
Oxides (%) –	1	2	3	4	5	6	7	8	
Major									
SiO ₂	44.45	36.2	27.45	32.34	29.95	31.48	31.59	25.35	
Al ₂ O ₃	10.52	18.49	19.94	24.44	24.45	19.32	20.36	17.77	
Minor									
Fe ₂ O ₃	21.22	17.38	20.25	15.44	17.85	20.34	18.34	5.53	
Na ₂ O	1.48	1.67	1.04	1.54	1.27	1.11	1.05	3.49	
K_2O	0.2	0.19	0.14	0.02	0.24	0.31	0.34	1.04	
MgO	4.31	4.27	5.55	4.3	4.99	2.56	5.36	8.73	
CaO	14.81	18.24	22	17.45	18.44	23.26	20.34	31.85	
MnO ₂	0.01	0.01	0.03	0.01	0.01	0.02	0.02	0.03	

	aior and minor elements in Th	ar coa
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ash $(23.16\% - 39.13\% \text{ SiO}_2, 7.66\% - 13.14\% \text{ Al}_2\text{O}_3, 1.94\% - 14.87\% \text{ Fe}_2\text{O}_3, 13.14\% - 18.39\% \text{ CaO}, 4.77\% - 6.44\% \text{ MgO}, 4.53\% - 6.61\% \text{ Na}_2\text{O}, and 0.40\% - 0.52\% \text{ K}_2\text{O})$ [20]. Chemical composition of Thar coal is also similar to the coal mine of Velenje, Slovenia with total moisture 38%, ash content 20%, heating value 3956 btu/lb, S 1.4\%, C 27.1\%, H 2.1%, O 11.0% and N 0.4\% [21]. The heating value of Thar coal is higher to a large extent than the lignite coal of Greece mined from the

basin of Megalopolis (1620 - 1980 btu/lb) and Ptolemais Basin (2070 - 2520 btu/lb) [22].

Thar coal has an advantage of low to moderate sulfur compare to the world's average sulfur (2.42%) in lignite coal [6]. Oxides of sulfur are the most concerned emission pollutants from the regulatory stand point. Low sulfur content in Thar coal makes it acceptable for power generation without exceeding the emission standard for sulfur oxides ($\leq 1\%$).

4. Conclusion

Thar coal has been ranked as lignite. SiO_2 and Al_2O_3 were identified as the major and Fe_2O_3 and CaO as the minor metal oxides in the ash residue. The surface of coal has been characterized by macro, meso and micropores with the irregular aggregates of minerals of calcium, sodium, potassium and aluminum. pzc of Thar coal ranges from pH 6.00 - 6.27. At this pH fines of coal float relatively easily, so the coal washing of low-rank coal of hydrophilic nature may work fast.

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REFERENCES

- A. Das, B. Sarkar and S. P. Mehrotra, "Prediction of Separation Performance of Floatex Density Separator for Processing of Fine Coal Particles," *International Journal* of Mineral Processing, Vol. 91, No. 1-2, 2009, pp. 41-49.
- [2] A. U. Kurniawan, O. Ozdemir, A. V. Nguyen, P. Ofori and B. Firth, "Flotation of Coal Particles in MgCl₂, NaCl, and NaClO₃ Solutions in the Absence and Presence of Dowfroth 250," *International Journal of Mineral Processing*, Vol. 98, No. 3-4, 2011, pp. 137-144. doi:10.1016/j.minpro.2010.11.003
- [3] X. Li, R. Shaw and P. Stevenson, "Effect of Humidity on Dynamic Foam Stability," *International Journal of Mineral Processing*, Vol. 94, No. 1-2, 2010, pp. 14-19. doi:10.1016/j.minpro.2009.10.002
- [4] K. S. Birdi, "Handbook of Surface and Colloid Chemistry," 3rd Edition, CRC Press, Taylor & Francis Group, Boca Raton, London, New York, 2009, pp. 655-679.
- [5] Y. D. Abreu, P. Patil, A. I. Marquez and G. G. Botte, "Characterization of Electroxidized Pittsburgh No. 8 Coal," *Fuel*, Vol. 86, No. 4, 2007, pp. 573-584. doi:10.1016/j.fuel.2006.08.021
- [6] V. Bouska and J. Pesek, "Quality Parameters of Lignite of the North Bohemian Basin in the Czech Republic in Comparison with the World Average Lignite," *International Journal of Coal Geology*, Vol. 40, No. 2-3, 1999, pp. 211-235. doi:10.1016/S0166-5162(98)00070-6
- [7] S. E. Kuh and D. S. Kim, "Effects of Surface Chemical and Electrochemical Factors on the Dewatering Characteristics of Fine Particle Slurry," *Journal of Environmental Science and Health. Part A: Toxic/Hazardous Substances & Environmental Engineering*, Vol. 39, No. 8, 2004, pp. 2157-2182. doi:10.1081/ESE-120039382
- [8] M. Kosmulski, "pH-Dependent Surface Charging and Points of Zero Charge. IV. Update and New Approach," *Journal of Colloid and Interface Science*, Vol. 337, No. 2, 2009, pp. 439-448. doi:10.1016/j.jcis.2009.04.072
- [9] M. N. Khan and A. Sarwar, "Determination of Points of

Zero Charge of Natural and Treated Adsorbents," *Surface Review and Letters*, Vol. 14, No. 3, 2007, pp. 461-469. doi:10.1142/S0218625X07009517

- [10] A. Sarwar, M. N. Khan and K. F. Azhar, "Kinetic Studies of Pyrolysis and Combustion of Thar Coal by Thermogravimetry and Chemometric Data Analysis," *Journal of Thermal Analysis and Calorimetry*, Vol. 109, No. 1, 2012, pp. 97-103. doi:10.1007/s10973-011-1725-0
- [11] R. C. Carpenter and H. Diederichs, "Experimental Engineering," 8th Edition, Wiley, New York, 1913.
- [12] M. Davranche, S. Lacour, F. Bordas and J. C. Bollinger, "An Easy Determination of the Surface Chemical Properties of Simple and Natural Solids," *Journal of Chemical Education*, Vol. 80, No. 1, 2003, pp. 76-78. doi:10.1021/ed080p76
- [13] The International Coal Encyclopedia, "Coal Services International," Vol. 1, Time off set Pte Ltd., 1990.
- [14] S. C. Tsai, "Coal Science and Technology Series 2: Fundamentals of Coal Beneficiation and Utilization," Elsevier Scientific Publishing Company, Amsterdam, 1982.
- [15] M. Shakirullah, I. Ahmad, M. A. Khan, M. Ishaq, H. Rehman and U. Khan, "Leaching of Minerals in Degari Coal," *Journal of Minerals & Material Characterization and Engineering*, Vol. 5, No. 2, 2006, pp. 131-142.
- [16] B. Manoj, A. G. Kunjomana and K. A. Chandrasekharan, "Chemical Leaching of Low Rank Coal and Its Characterization Using SEM/EDAX and FTIR," *Journal of Minerals & Materials Characterization & Engineering*, Vol. 8, No. 10, 2009, pp. 821-832.
- [17] K. H. Nimerick and B. E. Scolt, "New Method of Oxidised Coal Flotation," *Mining Congress Journal*, Vol. 66, 1980, pp. 21-22.
- [18] A. J. Rubin and R. J. Kramer, "Recovery of Fine-Particle Coal by Colloid Flotation," *Separation Science and Technology*, Vol. 17, No. 4, 1982, pp. 535-560. doi:10.1080/01496398208060257
- [19] K. Y. Zhang, H. P. Hu, L. J. Zhang and Q. Y. Chen, "Surface Charge Properties of Red Mud Particles Generated from Chinese Diaspore Bauxite," *Transactions of Nonferrous Metals Society of China*, Vol. 18, No. 5, 2008, pp. 1285-1289. doi:10.1016/S1003-6326(08)60218-6
- [20] B. C. Folkedahl and C. J. Zygarlicke, "Sulfur Retention in North Dakota Lignite Coal Ash," *Preprints Papers— American Chemistry Society, Division of Fuel Chemistry*, Vol. 49, No. 1, 2004, pp. 167-168.
- [21] J. Oman, A. Senegacnik and B. Dejanovic, "Influence of Lignite Composition on Thermal Power Plant Performance: Part 2: Results of Tests," *Energy Conversion and Management*, Vol. 42, No. 3, 2001, pp. 265-277. doi:10.1016/S0196-8904(00)00062-5
- [22] M. J. Galetakis and F. F. Pavloudakis, "The Effect of Lignite Quality Variation on the Efficiency of On-Line Ash Analyzers," *International Journal of Coal Geology*, Vol. 80, No. 3-4, 2009, pp. 145-156. doi:10.1016/j.coal.2009.092