

## Characterization of Khushab Coal (Punjab Pakistan)

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**Summary:** A coal sample obtained from Khushab District northern Punjab was characterized for various parameters of coal analysis. It was found from the ultimate and proximate analysis that fixed carbon is slightly above 40%, which shows that this coal has not reached its maturity and can be ranked between peat and lignite. It was also found that it contains about 2.98% total sulfur, which is an indication that it can be used for metallurgical purposes. The coal has been desulfurized with KOH, NaOH and HNO<sub>3</sub> and the sulfur percentage has decreased to 0.001%, 0.01% and 0.006% respectively with these leachants. Calorific value of virgin coal (untreated sample) has been found to be 6195 calories/g but has increased to 10448 calories/g after particularly being leached with (KOH).

The coal was also leached with hydrochloric acid and nitric acid to determine the leachability of these two acids for mineral elements such as copper (Cu), iron (Fe), calcium (Ca), magnesium (Mg), nickel (Ni), manganese (Mn), chromium (Cr) and cadmium (Cd). It was found that a very reasonable amount of these minerals could be extracted with these leachants.

### Introduction

Coal is abundantly available and is one of the main naturally occurring sources of energy. Coal as an energy source faces increasingly strict environmental constraints, worldwide now-a-days. The main problem associated with the burning of coal is the pollution of environment because highly contaminating gases are driven off during coal combustion. Various methods are being developed to make coal burning and other utilization environment friendly. Jianyu *et al*[1] have developed a new radiolytic desulphurization and bio-desulphurization method to make coal free from Sulphur dioxide production during combustion. Nagaoka *et al*[2] have also worked on the microbial desulphurization of organic and inorganic Sulphur in coal. Hussain *et al*[3] have analyzed a Turkish bituminous coal from a working floatation plant with the aim to determine quantitatively and semi quantitatively its clay mineral contents. Kong *et al*[4] have used computer controlled SEM

(CCSEM) to provide quantitative measurement of minerals in coal, including quartz, illite, kaolinite, montmorillonite, gypsum and some un-classified mixed elements. Korean anthracite coal was treated using molten caustic leaching (MCL) process and changes in their organic structure and combustion characteristics were investigated [5]. It was found that the changes in the combustion temperature and the reactivity after MCL treatment were attributed to the physical changes on the surfaces of organic groups. Mineral matters have also been determined in Degari coal [6] and Makarwal coal [7] to know about the minerals present in these coals. The present work deals with the characterization of khushab coal, because Pakistani coal is reluctantly used for power generation due to high ash, volatile matter and emission of noxious gases like SO<sub>2</sub> and H<sub>2</sub>S. There is a growing market for its large-scale utilization, particularly in power generation sector, but due to lack of reliable data on coal quality, coal

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reserves are not being fully exploited. An assessment of quality of these coals will help in attracting the users for coal based energy market. The present work is an attempt on this front. Khushab coal is the one, which needs characterization.

## Results And Discussion

### 1 Proximate Analysis

Results of Proximate analysis of coal under study are presented in Table 1. It can be seen that the moisture content is very low, the volatile matter contents are very high and the fixed carbon is low, which is indicative of the fact that this coal is young and immature. It can be ranked between peat and lignite. The lower, the fixed carbon, the lower is the rank of coal and the lower is the heating value.

Table-1: Determination of Moisture, Ash, Volatile Matter and Fixed Carbon in Coal Sample.

No	Parameter	Percentage
1	Moisture	4.75
2	Ash	20.4
3	Volatile Matter	33.75
4	Fixed Carbon	41.13
Coal Size	=	212-180 $\mu$ m
Sample	=	ROM (run of mine)
Room Temperature	=	~25°C.
Extraction Time	=	2 hours

Table 2 Ash contents in virgin and acid treated coal samples

No	Sample	Ash content%
1	Virgin coal sample	20.2
2	1M HNO <sub>3</sub> extracted sample	11.11
3	5M HNO <sub>3</sub> extracted sample	5.29
4	1M HCl extracted sample	10.8
5	5M HCl extracted sample	8.37
6	Mixture (3M HNO <sub>3</sub> + 3M HCl) extracted sample	3.09

Table 2 shows the ash content of virgin as well as the variously treated coal samples. It can be noticed that the ash content is 20% in virgin coal sample, but upon demineralization or extraction with acids like HNO<sub>3</sub>, HCl and their mixture, the ash content was reduced considerably. Determination of the ash content is of primary importance because it gives information about the carbonaceous material and mineral contents of the coal. High ashes are undesired because of its deleterious effect on coal utilization processes like liquefaction, combustion and gasification. High ash may cause poisoning effect and passivate the

catalysts. More over high ash contents of the coal may lead towards agglomerate formation during combustion and thus causing corrosion of the metallic parts of combustion appliances, particulate emissions (fly ash), and dust nuisance in the vicinity of coal combustion plants.

Table-3: Total Sulfur in Virgin Treated Coal Samples

No	Sample	Total sulfur %
1	Virgin coal sample	2.98
2	NaOH extracted sample	0.001
3	KOH extracted sample	0.01
4	HNO <sub>3</sub> extracted sample	0.006
Coal Size	=	212-180 $\mu$ m
Sample	=	ROM
Room Temperature	=	~25°C.
Extraction Time	=	2 hours

### 2. Determination of Sulfur

Table 3 shows total sulfur determined in the virgin and acid extracted coal sample. The sample was extracted with bases like sodium hydroxide, potassium hydroxide and acid like HNO<sub>3</sub>, which have the ability to desulfurize the coal [9]. It was observed that this treatment caused a significant decrease in the total sulfur content of the coal. Amongst these reagents potassium hydroxide caused a maximum reduction of sulfur. The reason might be that KOH and NaOH has the ability to cleave certain weak linkage in the coal like (R-SR) or (R-O-R). Our results are in good agreement with the earlier results that desulfurization can be achieved by treating coal with these alkali, [10-14]. Nitric acid also caused a significant reduction in the sulfur content. The reason might be that nitric acid has the ability to extract pyretic sulfur like FeS, ZnS or PbS as earlier has been reported [15,16]. Sulphatic sulfur in virgin as well as variously treated coal sample have been given in Table 4, here also treatment with these reagents have caused a reduction in sulfatic sulfur with maximum in case of nitric acid. However, compared to the total

Table-4: Determination of the Sulfatic Sulfur in Virgin as well as Variously Treated Coal Samples.

No	Sample	Sulfatic sulfur %
1	Virgin coal sample	0.214
2	KOH extracted sample	0.06
3	NaOH extracted sample	0.15
4	HNO <sub>3</sub> extracted sample	0.03
Coal Size	=	212-180 $\mu$ m
Sample	=	ROM
Room Temperature	=	~25°C.
Extraction Time	=	2 hours

sulfur, all these reagents caused minimum extraction of the sulfatic sulfur. The reason might be that the sulfatic sulfur exists as  $\text{CaSO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{MgSO}_4$ . So during extraction equilibrium may perhaps be established between the extracted sulphate ion and the metal ion. Chlorine was also determined in the virgin coal, which was 0.22%.

Table-5: Calorific Values of the Virgin and Treated Coal Samples

S No	Sample	Calories/gm
1	Virgin coal sample	6195
2	NaOH extracted sample	7777
3	KOH extracted sample	10448
4	$\text{HNO}_3$ extracted sample	7046

Coal Size = 212-180 $\mu\text{m}$   
 Room Temperature = ~25°C.  
 Extraction Time = 2 hours

### 3. Calorific Value

Table 5 shows the heat contents or the calorific values of the virgin as well as the treated coal samples. It is clear from the table that the heating values of the treated coal have been increased comparing with that of the virgin, while a maximum increase can be noticed with KOH treatment. The reason might be the removal of non-carbonaceous materials or mineral matter with these treatments which have no heating value and which

can catalyze certain endothermic reaction during combustion like Boudoward reaction.



Thus the mineral matter depletion caused by treatments with alkali and acid might have caused enhancement in the heat content or the calorific value. The calorific value is an important assessment test. The higher is the calorific value the good is the quality of the fuels.

### 4. Leaching Effect of Nitric Acid

Leaching effect of nitric acid (different molarities) on the extraction of various metals like copper (Cu), Iron (Fe), calcium (Ca), magnesium (Mg), nickel (Ni), manganese (Mn), Chromium (Cr), and Cadmium (Cd) is provided in Figure 1. It can be observed that copper extraction is maximum with 1M  $\text{HNO}_3$  and minimum with 3M  $\text{HNO}_3$ . The reason might be that Cu occurs in coal mainly in the form of  $\text{CuFeS}_2$  [17]. As the role of nitric acid for the removal of pyretic sulfur is well established [15]. Thus the Cu have easily been extracted with this treatment. The reason for maximum extraction with 1M  $\text{HNO}_3$  might be the pH of the slurry, which makes removal easy. At this very pH, the extractant is able to achieve maximum imbibitions into the

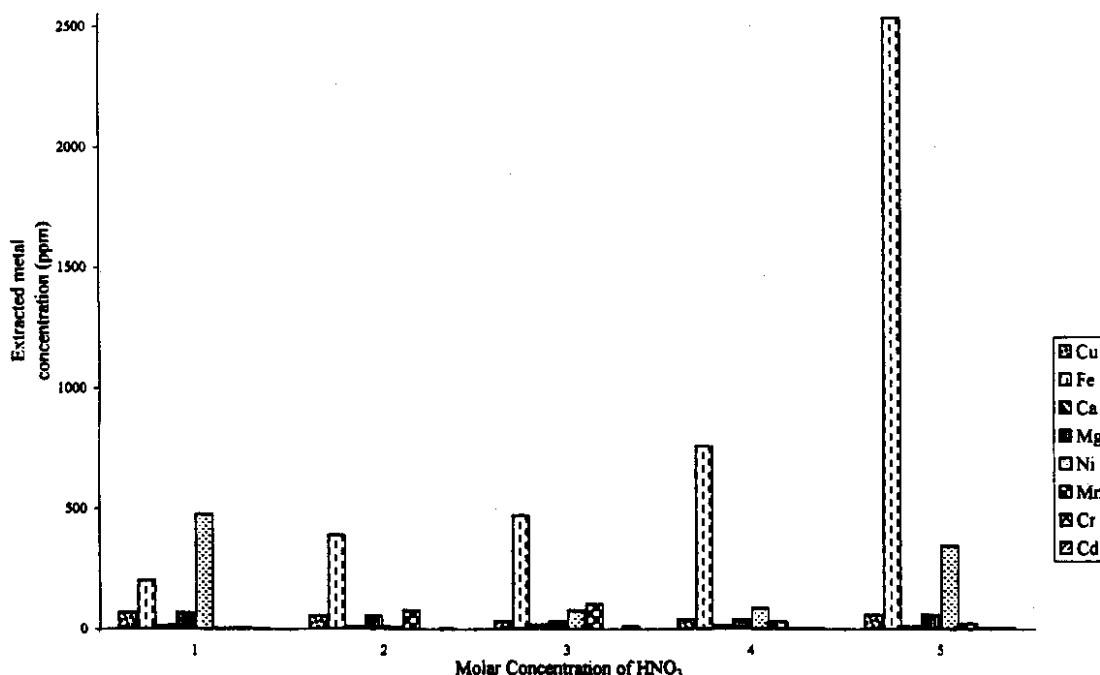


Fig 1: Extraction of Metals with different concentration of  $\text{HNO}_3$ .

coal micro pores. The effect of concentration of nitric acid on extraction of iron can be seen from the displayed figure. It's evident that extraction of iron is low up to 4M concentration of HNO<sub>3</sub> but with 5M nitric acid, the extraction attains maximum value. Moreover compare to Cu, Fe was extracted appreciably with HNO<sub>3</sub>, particularly with 5M HNO<sub>3</sub>, Which is in conformity with the earlier work that Fe (Pyrite) can be extracted with HNO<sub>3</sub> appreciably compared to other extractants [12].

The extraction of Ca with different molarities of nitric acid is also appreciably high with all of these treatments particularly with 3M HNO<sub>3</sub>. The reason might be that Ca is a lithophillic metal and present in coal in the form of discrete mineral matter [17]. Thus their removal with acid treatment is easy compared to the removal of organically bound mineral or metal porphyrins.

The extraction of Mg, leached with nitric acid is appreciably high with all these treatments, the maximum extraction has been achieved with 3M HNO<sub>3</sub>. Again the reason for the maximum extraction is that this metal is also lithophillic and can be introduced into the coal seam from the surrounding. Thus it exist in the form of discrete minerals in the coal [17], which can be extracted easily with acid treatment and even with water. The maximum extraction with 3M HNO<sub>3</sub> is due to the pH of the slurry. At this pH, magnesium (Mg) like Ca and Fe was extracted appreciably.

The concentration of Ni, Mn, Cr and Cd leached with different molarities of nitric acid is very low. The origin of these metals may be inherent or they may be introduced into coal during coalification from the surrounding via the agency of rainwater. Extraction of these trace metals with different molarities is not so profound like extraction of Fe, Ca and Mg. Variable amounts of metals extracted with different molarities of the acid might be due to the heterogeneity of the sample.

The results compiled in Figure 1 reveal that lithophillic metals can be appreciably extracted with nitric acid compared to chalcophyllic and trace metals.

### 5. Leaching Effect of Hydrochloric Acid

In order to enhance the leaching of the chalcophyllic and trace metals, the extraction medium was changed and the leaching was

performed with different molar solutions of hydrochloric acid. The concentration of Fe ( $\mu\text{g/g}$ ) leached with different molarities of hydrochloric acid is provided in Figure 2. The effect is not so pronounced as compared to nitric acid. It confirms the earlier proposition that Fe exist, in coal as FeS<sub>2</sub>, which can be effectively removed with HNO<sub>3</sub> acid. Again it can be seen that the effect of molarities of the extractants is not so marked except 1M concentrations where maximum extraction was achieved. The reason might be the equilibrium, which is established between the extraction and re-adsorption and also the heterogeneity of the sample under study.

The effect of concentration of hydrochloric acid on extraction of Calcium (Ca) is also provided in Figure 2. Again the extractability of Ca is surprisingly low compared to that with nitric acid. As Ca exists in coal in the form of discrete mineral matter (carbonates), which can be effectively extracted with HCl. However the results are not in good agreement with this proposition. The concentration of magnesium leached with different molarities of hydrochloric acid have been provided in Figure 2. The extraction trend is compitible with that of nitric acid. As Mg exists in coal in the form of discrete mineral form which can effectively be extracted or leached with hydrochloric acid as well as with nitric acid. It can be seen from the figure that like nitric acid, hydrochloric acid also caused maximum extraction of magnesium.

The leachability trends of other trace metals like copper (Cu), nickle (Ni), manganese (Mn), chromium (Cr) and cadmium (Cd) with varying concentration of hydrochloric acid have also been provided in Figure 2. It can be seen that these metals are not extracted appreciably with this treatment compared to HNO<sub>3</sub> extraction. The reason might be that these metals exist either in the form of ion-exchangeable cation attached directly to the organic matrix of coal or they may exist in trace metals. As coal is a porous material and composed of macro and micro pores, thus the lower extraction caused by hydrochloric acid as well as by nitric acid might be due to the diffusion limitations. The pores are so narrow or mainly blind that the extractant is unable to admit into these pores, thus causing reduction in its extractability or leach ability.

It may be concluded from the analysis of the Khushab coal that it contains less amount of sulfur and chlorine and that because of the high volatile

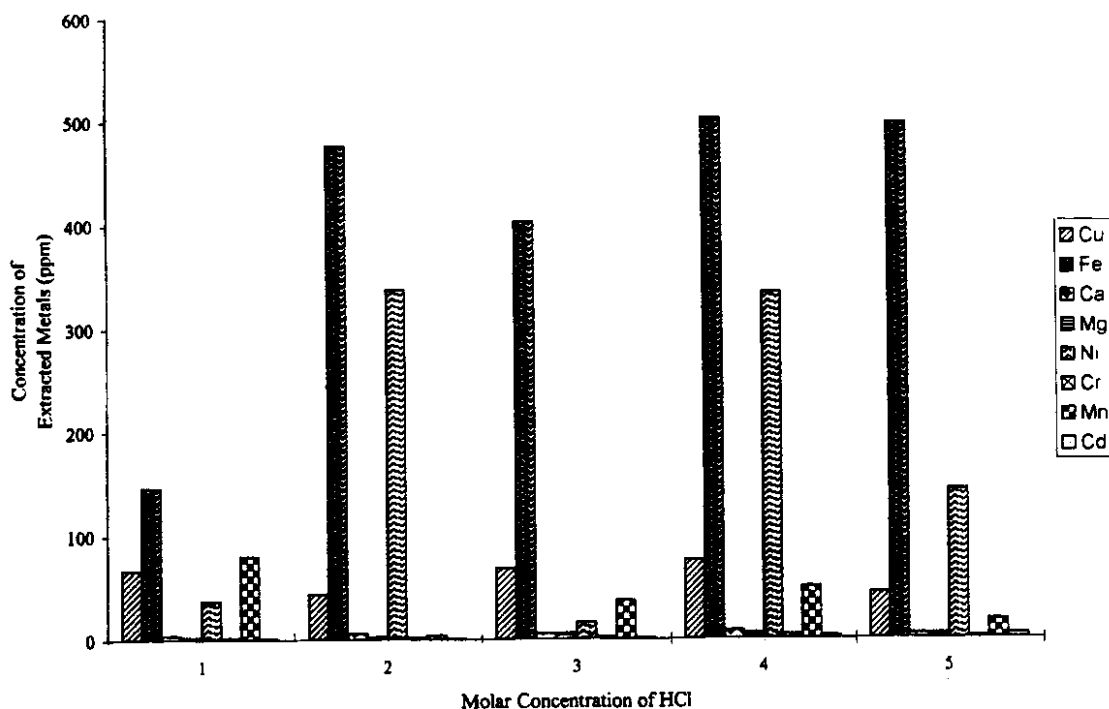


Fig 2: Extraction of Metals with different concentration of HCl.

matter and low fixed carbon, this coal is considered as immature which can be ranked between peat and lignite. However in comparison with other Pakistani coals, the mineral matter present in it can be leached with extractants like  $\text{HNO}_3$  and  $\text{HCl}$ . Its sulfur contents can be controlled with reagents like  $\text{NaOH}$  and  $\text{KOH}$  to a greater extent. Based on the experimental findings, this coal can compete with other Pakistani coals and can share its role in minimizing the country's energy problems getting worsened day by day.

### Experimental

A small portion from the representative coal sample was crushed to pass through 212-180  $\mu\text{m}$  sieve. Proximate analysis of the coal was carried out according to the established method [8]. Sulfur contents were also determined using the same method. Calorific value of the sample was determined with bomb calorimeter (Gallenkamp)

Inorganic elements were determined in the coal by atomic absorption spectrophotometer. Samples for this analysis were prepared in such a way that 100ml of different molar solutions of  $\text{HNO}_3$  and  $\text{HCl}$  were taken in separating funnels and 1-gram coal sample weighed in filter paper for

each case was placed in funnel. The acid solution was drop wise percolated through the coal slowly to leach out mineral matters present in coal. The filtrate, collected in the beaker, was stored in polythene bottle for metal analysis.

### References

1. N. Jianyu, and Y. Hong, *Dizhi Digiu Huaxe*, **3**, 64 (1997).
2. Nagaoka, Toru, Ohmura, Naoya and Saiki, Hiroshi, *Ryusan to Kogyo* **51**(1), 6 (1998).
3. S.A. Hussain; G, Ozbayoglu, and S., Demirci, *Chem. Acta. Turc, sold* **25** (2), 59 (1997).
4. K. Lingbu, J. Zygarlicke, C. Benson and A. Steven A. Proc-annu. Int. Pittsburgh Coal Conf. 13<sup>th</sup> (Vol.1) 222 (1996).
5. L. Sihyun; S. Euxykwon and P. Seok Proc. Annu. Int. Pittsburgh Coal Conf. 12<sup>th</sup>, 499 (1995).
6. M. A. Khan, M. I. Mohmand and Khadim-ul-Faqir, *J. Chem. Soc. Pak.* **9**(2) (1987).
7. M. Ishaq, M. Arsala Khan and Yousaf Iqbal, *Scientific Khyber*, **14** (1) 59 (2001).
8. J.H. Harker, "Fuel and energy" Academic press, (1981).
9. Katsuki Kusakabe, *Fuel*, **68**, 396-399, (1989).
10. R.A. Meyers, in "Coal Desulfurization"

- Merzel Dekker, New York, (1977).
11. P.Chioti,, and R. Markuszewski, *Ind. Eng. Chem. Process Ind. Eng. Chem. Process Des. Dev.*, **24**, 1137, (1985).
  12. P.X. Masciantonio, *Fuel*, **44**, 269, (1965).
  13. D.J. Boron, and R. Kollrack, *Mining Eng.*, **38**(2), 120. (1986).
  14. J.T. Riley, and G.M.Ruba, *Fuel*, **68**, 1594 (1989).
  15. H.J.Gluskoter, *Energy Sources*, **3**(2), 125 (1977).
  16. J.N.Chakrabati, in "Analytical Methods for Coal and Coal Products" **1**, p.279, Academic Press, New York, (1978).
  17. J.A.Minkin, *Am. Chem. Prepr*, **24** (1), 242 (1979).