

## Vat Leaching of Bulk Mineral Matter from Some Pakistani Coals Effect of Leachant Concentration

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**Summary:** Effect of leachant concentration on mineral depletion in some Pakistani coals was studied varying the concentration of leachants i.e. Ammonium acetate, HCl, HNO<sub>3</sub> and HCl followed by HF followed by HCl. The extracts as well as the residual coal samples were analyzed for inorganic elements i.e. Fe, K, Na and Ca+Mg (combined). Amongst the metals studied, Fe and Ca+Mg have been extracted significantly compared with the extraction of Na and K. Complete mineral depletion in any case was not achieved even when extraction was performed with high concentration of either of the leachants. Leachability of some metals has been found concentration dependent while other exhibited deviation.

### Introduction

The day-by-day hike in price as well as dwindling and unreliable supplies of petroleum-based oil diverted the world's attention towards the use of coal. Though coal is a precious commodity but users are reluctant due to high ash, and sulfurous & fugitive emissions associated with its use. Ash which mainly constitute minerals creates problems of agglomerates and hence corrosion of the metallic parts of the combustor. More over it may cause environmental pollution when get elutriate as fly ash and also pollute under ground water aquifers if carelessly disposed. Coal ash has been declared unwanted in conversion of coals to synthetic fuel which where in cause passivation of the catalyst [1-5]. Thus coals are not in compliance with the recent requirements; hence require some cleaning to meet environmental legislations. Extensive work is under way world wide on the beneficiation and demineralization of the coal to make it a clean burning fuel [6-10] for an emerging coal based market for power generation hoped after the shrinkage of petroleum based oils.

### Results and Discussion

The amount of inorganic elements leached with 1M and 5 M ammonium acetate for time duration of 2-0 hr is provided in Fig.1. Extraction with this treatment was performed with the objectives to remove ion-exchangeable elements present as cations [11]. The present work was undertaken to analyze lithophillic metals like Ca+Mg (combined), Fe, K and Na due to their frequent detrimental and toxic effects when present in appropriate concentrations. These metals are believed to be

present mainly in discrete and organically based form. It is evident from the figure, that leaching of some of the metals with 1M-ammonium acetate is quite low compared to the virgin coal ash. Amount of metals like Fe (827, 623, 2818 and 728 µg/g), Ca+Mg (3200, 5440, 3840, 3840 µg/g), Na (760, 1324, 999, 1803 µg/g), and K (25, 39, 129 and 52 µg/g) determined in Makarwal, Degari, Shahrigh and Sor range coals respectively is significantly low compared to virgin samples. This is suggestive of the fact, that these elements may be present partly as directly bound to the organic matrix in an ion exchangeable form and partly as part of discrete mineral phases. Amongst Mg and Ca, magnesium prefers to form six co-ordinate compounds of regular octahedral geometry with the sites in coal but Ca, being a larger cation is able to accept higher co-ordination numbers and irregular geometries. The greater flexibility of Ca for binding sites allows it to function more effectively than Mg<sup>+2</sup> to negatively charged sites, as these sites provide an irregular geometry. Presence of inorganic elements attached directly as ion exchangeable cations to the organic coaly matter and those in association with discrete mineral matter have been reported elsewhere. [12,13]. Extraction with this treatment might have caused extraction of inorganic elements associated as ion exchangeable cat ion with organic matrix as well as discrete mineral phases housed or captive in pores.

Extraction of various metals with 5M-ammonium acetate for time duration of 2-0 hrs was also performed. The data is plotted in Fig. -1. It is evident that Fe (1940 µg/g) has significantly been

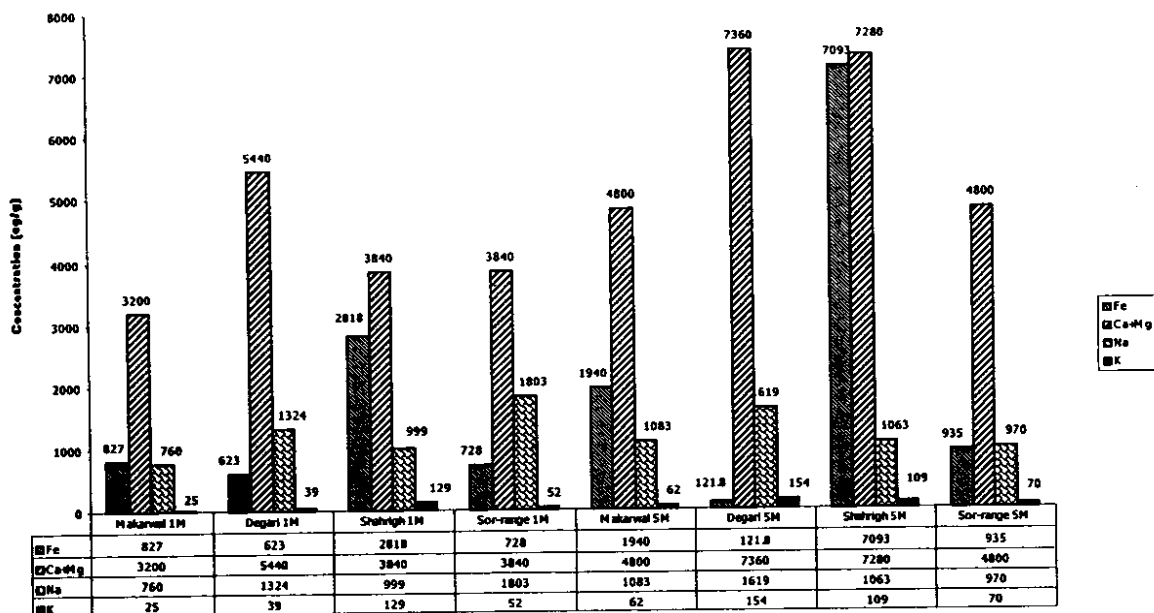


Fig. 1 Amount of Inorganic Elements ( $\mu\text{g/g}$ ) determined in Leachates with 1M & 5M Ammonium Acetate.

extracted in case of Makarwal coal, where as in other cases, it has reduced (from 3658-213  $\mu\text{g/g}$  in case of Degari coal and from 12730-3820  $\mu\text{g/g}$  in case of Shahrigh coal) compared to its values extracted with 1M-ammonium acetate. Fe is the transition metal, which adopt alternative coordination number and geometry compared to  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$ . It occurs in a range of oxidation states to allow the ready transfer of electrons to the binding site. Amount of Ca+Mg (4800, 7380, 7280 and 4800  $\mu\text{g/g}$  determined in Makarwal, Degari, Shahrigh and Sor range coals respectively) has decreased in leachates with 5M compared to that with 1M-ammonium acetate in case of all coal samples where it has increased. Amount of Na (1083, 1619, 1063, 970  $\mu\text{g/g}$  in case of all coals), K (62, 154, 109, 70  $\mu\text{g/g}$  in case of all coals), has not altered much with 5M -ammonium acetate, thus concentration of the leachant has profound effect on the extraction of metals like Fe, & Ca+Mg, while meaningless in cases of Na and K in all coal samples.

The amount of inorganic elements extracted with 1M and 5M HCl for time duration of 2.0 hrs is provided in Fig-2. Na (from 122-955  $\mu\text{g/g}$  in case of Makarwal coal), and K (258-1461 $\mu\text{g/g}$  in case of Shahrigh coal) have increased in some samples where as decreased in others (Na from 1513-730 $\mu\text{g/g}$  in case of Shahrigh coal and K from 1154-51 $\mu\text{g/g}$  in case of Makarwal coal). It was expected that HCl

would have extracted greater amount of Ca by reacting with  $\text{CaCO}_3$  present in coal. However the results are not in good agreement with the expected one. Because of their weak interaction with sites in coal (Particularly in case of  $\text{Na}^+$  and  $\text{K}^+$  due to their poor polarizing power), they prefer to bind to oxygen donor sites and many of their salts are insoluble and precipitate as carbonate, phosphate and oxalate. It can be seen that the effect is not noteworthy. Some elements have increased in one sample where as in another coal sample their amounts have decreased. This may be due to readsorption of some of the elements from the extracting solution. Amount of Fe and Ca +Mg have increased significantly with HCl in all samples.

Fig.3 shows the extraction of coals with 1M and 5M  $\text{HNO}_3$  for time duration of 2.0 hrs. It can be seen that concentration of leachant has no effect in some cases while profound in other cases. Amount of Ca+ Mg (from 7040 to 8000  $\mu\text{g/g}$  in case of Shahrigh coal and from 5780 to 7380  $\mu\text{g/g}$  incase of Sor range coal) has increased with increase in concentration of the leachant in case of Shahrigh and Sor-range coal samples. A decrease can be noticed in amount of Ca+Mg (from 6080 to 4480  $\mu\text{g/g}$  in case Makarwal coal and from 10580 to 9920  $\mu\text{g/g}$  in case of Degari coal sample) upon increase in concentration of  $\text{HNO}_3$ . Effect of concentration on the extraction of Fe

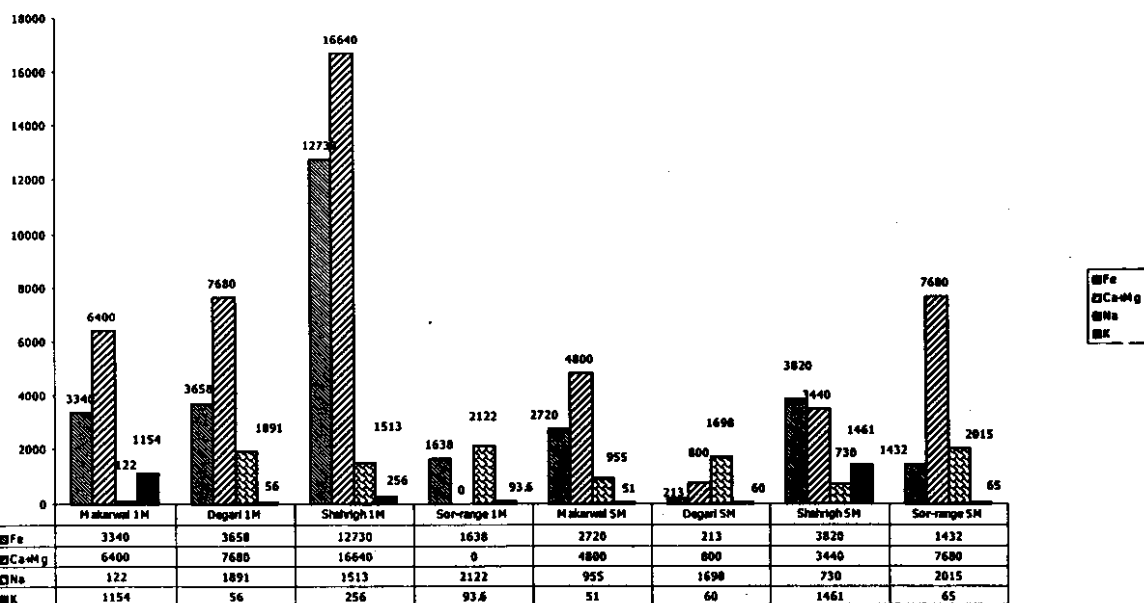


Fig. 2 Amount of Inorganic Elements ( $\mu\text{g/g}$ ) determined in Leachates with 1M & 5M Hydrochloric Acid.

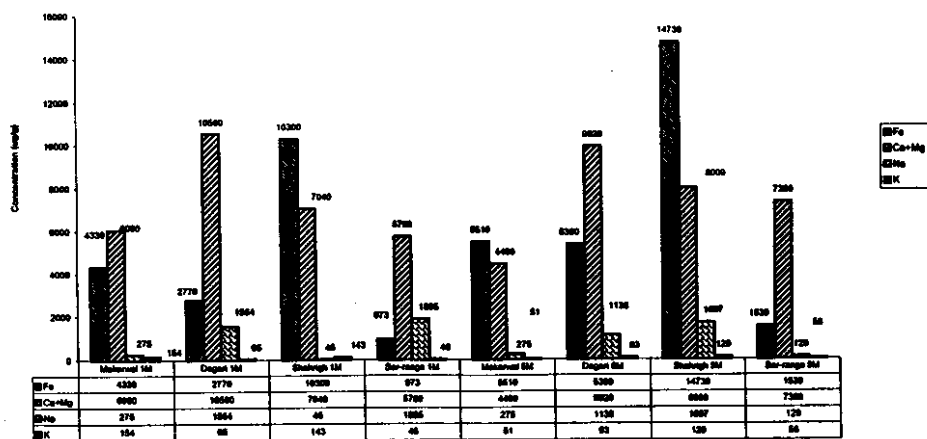


Fig. 3 Amount of Inorganic Elements ( $\mu\text{g/g}$ ) determined in Leachates with 1M & 5M Nitric Acid.

noticeably high in all cases. The amount of organic elements extracted with  $\text{HNO}_3$  when compared with  $\text{HCl}$ , shows that extraction of Fe is significantly high with  $\text{HNO}_3$  compared to that with  $\text{HCl}$  in all four-coal samples. It has been reported earlier that pyrite ( $\text{FeS}_2$ ) can be extracted with  $\text{HNO}_3$  and not with  $\text{HCl}$  [14]. Thus high extraction of Fe with  $\text{HNO}_3$  can be ascribed to pyritic iron. Maximum extraction of Fe with chemical treatments has already been reported [15, 16]. Extraction of other elements have affected differently in different coal samples with  $\text{HNO}_3$  compared to that with  $\text{HCl}$ . Some

elements have attained maximum extraction while others minimum.

Fig.4 shows extraction with 1M and 5M  $\text{HCl}$  followed by  $\text{HF}$  followed by  $\text{HCl}$  treatment. Extraction with this treatment was expected to completely demineralize the coals. Silica and clays could be effectively removed with  $\text{HF}$ . It is clear from the displayed data that concentration has positive effect on the extraction of Fe (from 1287-1696  $\mu\text{g/g}$  in case of Makarwal coal) and  $\text{Ca} + \text{Mg}$  (from 1920-3520  $\mu\text{g/g}$  in case of Makarwal coal).

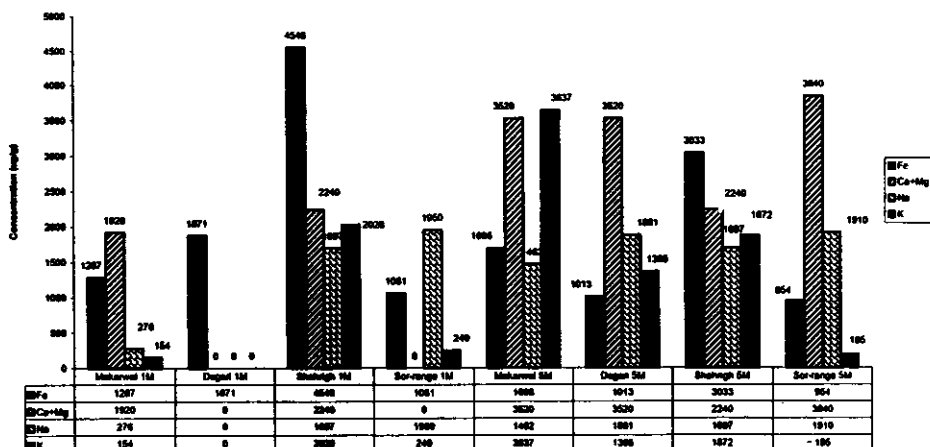


Fig. 4 Amount of Inorganic Elements ( $\mu\text{g/g}$ ) determined in Leachates with 1M & 5M HCl followed by HF followed by HCl.

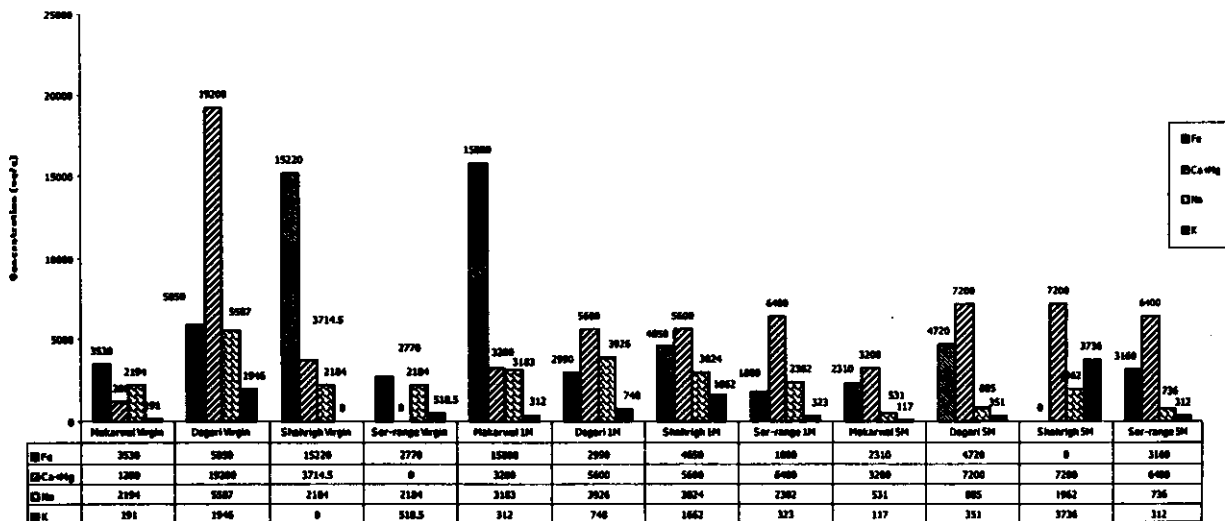


Fig. 5 (a) Amount of Inorganic Elements ( $\mu\text{g/g}$ ) Determined in the Ashes of Virgin and 1M & 5M  $\text{CH}_3\text{COONH}_4$  extracted Residual Coals.

However other elements have affected differently. Extraction of other elements has either decreased or increased in case of other coal samples.

highest amount of Fe and Degari has the highest amount of Ca+Mg.

Fig. 5 (a, b, c, d) show the amount of various inorganic elements determined in the ashes of virgin as well as residual coal samples. The data plot shows that in the ashes of all four virgin coals, elements like Fe, K and Ca+Mg are present in appreciable amount which is suggestive of the fact that neither ammonium acetate nor acids, and their mixture caused complete demineralization. It was found that amongst the four coals studied, Shahrigh has the

It can be seen that amount of various elements in the ashes of demineralized residual coal samples is quite significant. Most of them have not been removed completely even though their amount in most instances has reduced appreciably. Complete removal of mineral matter from coal thus requires successive treatments with various acids, especially with HCl followed by HF followed by HCl. Concentration of extractant may not have appreciable effect on extraction due to establishment of,

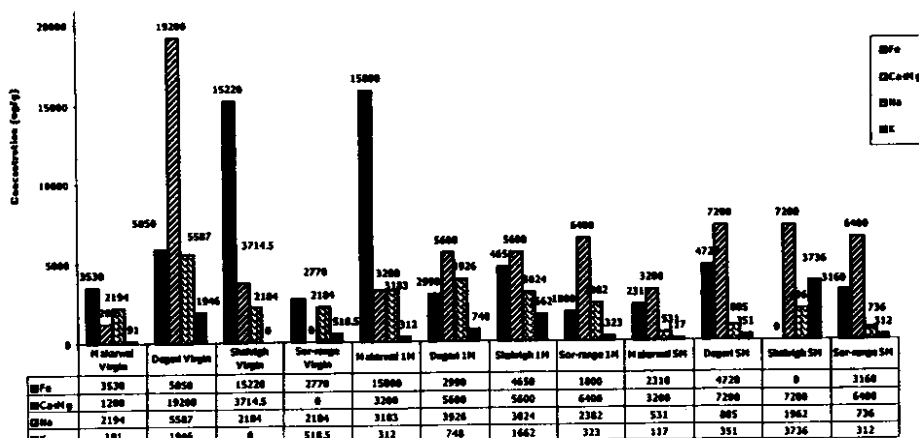


Fig. 5 (b) Amount of Inorganic Elements ( $\mu\text{g/g}$ ) Determined in the Ashes of Virgin and 1M & 5M HCl extracted Residual Coals.

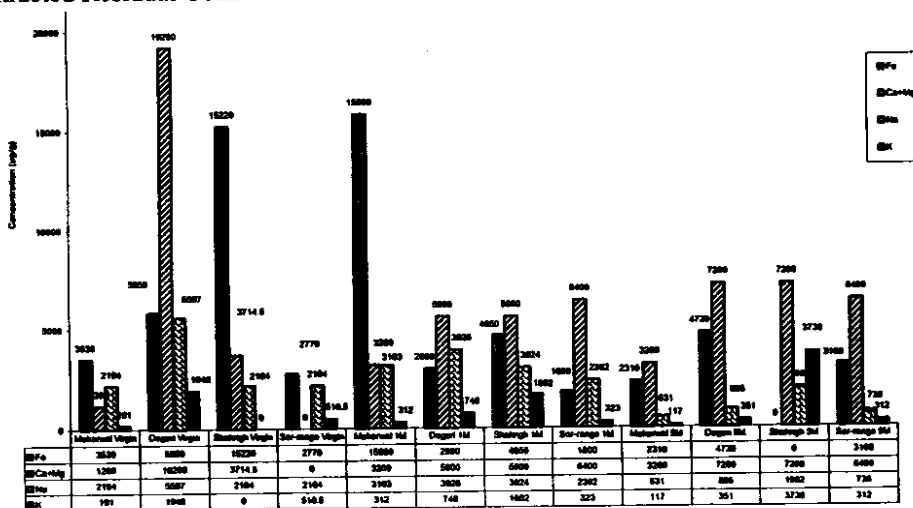


Fig. 5 (c) Amount of Inorganic Elements ( $\mu\text{g/g}$ ) Determined in the Ashes of Virgin and 1M & 5M  $\text{HNO}_3$  extracted Residual Coals.

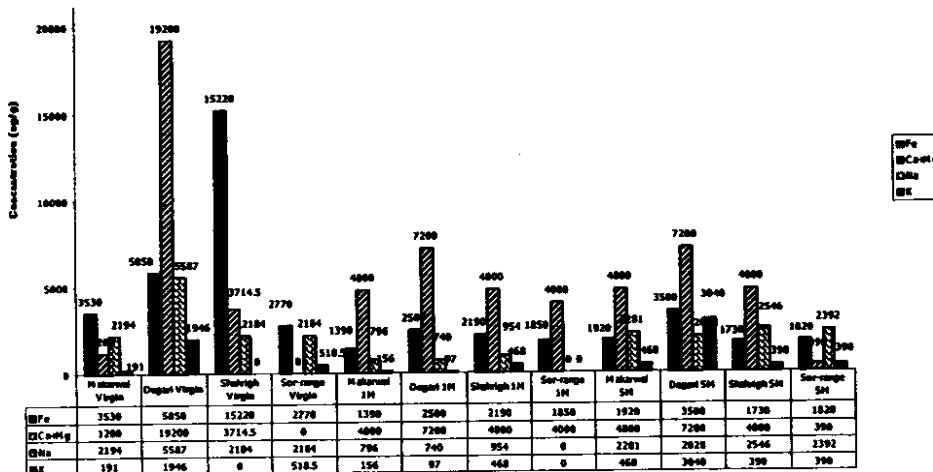


Fig. 5 (d) Amount of Inorganic Elements ( $\mu\text{g/g}$ ) Determined in the Ashes of Virgin and 1M & 5M HCl + HF+HCl extracted Residual Coals.

equilibrium between desorption and readsorption to the chelating sites.

## Experimental

### Preparation of Coal Samples

Run of mine samples were obtained from Makarwal, Sor-range, Shahrigh and Degari coal mines, crushed in a pistle and mortar, sieved using screen 250 and 212  $\mu\text{m}$ . The particles through 250 screen and retained on 212 micrometer were used. The definite sized samples were dried in vacuum at 70°C and stored. The proximate and ultimate analysis of coals samples understudy are provided in Table 1 A & B.

Table 1-A: Proximate analysis of coals understudy

Coal Sample	Moisture	VM	Ash	Fc
Sor range*	14.7	36.4	7.1	41.8
Degari*	12.1	35.5	18.0	34.4
Makarwal**	3.6	37.6	20.8	38.0
Shahrigh*	10.6	25.9	19.8	33.7

Table 1-B: Ultimate analysis of coals understudy

Coal Sample	Carbon (%)	Hydrogen (%)	Sulphur (%)	Chlorine (%)	Calorific Value (Btu/lb)	
					Gross	Net
Sor range*	51.2	4.1	5.0	0.02	9969	9431
Degari*	50.9	4.2	2.2	0.02	8840	8326
Makarwal**	-	-	6.11	0.08	10065	-
Shahrigh*	51.2	3.9	4.0	0.01	8764	8290

\* Analyzed by Holderbank A.G. Switzerland.

\*\* N.C.B. Yorkshire Regional Laboratory, U.K.

Source: Chemical consultant (Pakistan) Ltd., 1984.

VM: Volatile Matter

FC: Fixed Carbon

### Extraction Procedure

Five grams portion of each of the already prepared coal samples was taken in Erlenmeyer flask. 50-cm<sup>3</sup> portion of 1M extractant was added. The slurry was stirred for time duration of 2-0 hrs at 50 °C using a magnetic stirrer and then filtered. The residual coal was exhaustively washed till free of extractant with hot deionized water. The filtrates were evaporated to a constant volume of 200cm<sup>3</sup> and kept in polyethylene bottles for metal determination. The residual coal was dried in vacuum oven at 70 °C and stored. The same procedure was adopted for treatment of coal with 5M HCl, HNO<sub>3</sub> and HCl followed by HF followed by HCl.

separately dissolved in acid mixture made of H<sub>2</sub>O : HNO<sub>3</sub>: HCl : HF in a molar ratio of 10:5:1:1, filtered, the leachates were diluted to 100 cm<sup>3</sup> with deionized water in polyethylene bottles.

### Analysis

Fe was analyzed by potassium thiocyanate method using a double beam shimadzu UV-visible 160 A Spectrophotometer. Ca +Mg (combined) using Eriochrome Black T indicator and Na and K by flame photometry.

### Conclusions

It is concluded from this study that vat leaching of lithophillic metals like Fe, Ca+Mg, Na and K is possible with these leachants. However complete leaching is impossible with either of leachants. Concentration of leachant has no profound effect on the removal of all the metals under study, though in some cases, leachability was found

concentration dependent. This is due to the fact that the metals has perhaps organic affinity and hence are difficult to be extracted. The mineral matter present as discrete lenses particularly Fe & Ca+ Mg were appreciably extracted with either of the extractant. For maximum extraction of organically based minerals heap, dump or in-place leaching is thus suggested instead of increasing the molar concentration of the leachant. For maximum extraction of these metals, extended time leaching is also suggested. Another reason of variation in the results is the sulphur contents of coals understudy, which in turn exacerbated the leaching.

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In second step one-gram portion of virgin as well as variously extracted coal residues were ashed at 750 °C in a muffle furnace. The ashes were

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