WASHABILITY STUDY OF FOUR PAKISTANI COALS BY FLOAT AND SINK TECHNIQUE-II

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ABSTRACT

Various Pakistani coal samples were separated into float and sink fractions using media of different specific gravities. The various float and sink fractions as well as the whole coal samples were ashed at 750 °C in a muffle furnace and the ashes were analyzed for Co, Cu, Ni, and Zn by atomic absorption spectrophotometer. The results showed that less enrichment of these metals occurred in the sink fraction in media of different specific gravities in case of Makarwal and Sor-Range coals. However, in case of Degari and Shahrigh coals considerable enrichment of these metals occurred in the sink fractions. The results were explained by suggesting that in case of Makarwal and Sor-Range coal samples, considerable amounts of these trace metals might occur in close association with the organic structure of coal which are difficult to be removed by the specific gravity method of coal cleaning. In case of Degari and Shahrigh coals, however considerable amounts of these metals might occur as discrete minerals matter which can be separated with ease from coal by the specific gravity method of cleaning.

Keywords: *Coal, Trace metals, Float - sink separation*

1. INTRODUCTION

Coal is a heterogeneous substance and is composed of a combustible organic matter and a noncombustible inorganic matter. The organic matter is present in the form of macerals whereas the inorganic matter is present in the form of mineral matter. Mineral matter in coal has several fold implications. Coal containing high mineral matter or ash forming material is considered low quality coal. High mineral matter in coal causes fire tubes agglomeration, fouling, sintering and corrosion during combustion for power generation. The mineral matter in coal also has adverse environmental effects.

Previous studies have shown an increase in the concentration of toxic trace elements in the biosphere resulting from coal combustion processes which have a negative impact on plant, animal and human life [1, 2]. Beneficial effects of mineral matter have also been reported in coal liquefaction processes [3].

Extensive work has been reported in literature worldwide on the trace metals content of different coals and their mode of occurrence. A wide variation in trace metal content from the same coal mine and even in the same seam has been reported [4]. The concentration and mode of occurrence of trace elements depend on a complex set of geological interactions between the intake of trace elements during

plant growth, enrichment during plant decay, sedimentation and diagenesis, burial and coalification and late stage mineralization [5] A generalized view of some Chinese coal, USA coals and world average has been given by Dai *et al* [6] Ketris and Yudovich [7] estimated world averages for trace elements in coal.

Trace elements in coal are present as main or trace components of discrete mineral phases, as adsorbed elements in inorganic materials and as part of the organic coaly structure in the form of organometallics, chelates or ion-exchangable compounds [8]. The present study concerns only with the trace metals present in coal and their beneficiation in media of different specific gravities.

The organic and inorganic association of trace metals in coal is a subject of great interest from coal utilization, coal cleaning and environmental point of views .Extensive literature is available on the subject. Float – sink separation of coal samples has been used as a viable tool for speciation of trace elements as whether they are organically bound in the coal matrix or present as part of discrete mineral particles. Based on float-sink analysis of coal in media of different specific gravities, Zubovic [9], listed the percentage organic affinity of some trace elements as: Ge (87), Be (82), Ga (79), Ti (78), B (77), V (76), Ni (59), Cr (55), Co (53), Y (53), Mo (40), Cu (34), Sn (27), La (3) and Zn (0). Gluskoter [10] separated four coal samples into a series of specific gravity fractions. The various fractions were then analyzed for trace metals. The trace metals were listed in a table in order of decreasing organic affinity. He categorizes the elements into the following four groups: Elements with greatest organic affinities (Ge, Be, B), inorganically bound elements (Hg, Zr, Zn, As, Cd, Pb, Mn, and Mo), elements closely associated with the elements having strong organic affinities (P, Ga, Sb, Ti, and V)

and elements closely associated with the elements having strong inorganic affinities (Co, Ni, Se, Cr, and Cu).

Swaine [11] suggested association of trace elements with carboxylic, phenolic, hydroxyl, mercapto, and imino groups in coal structure.

Ward [12] used float and sink fractions of six Australian coals for trace metals and found B, Ni, V, Zr, Co, and Be as having organic affinity, Cu, Pb, Zn, Mo, Sr, and Cr as having inorganic affinity, whereas Ge as having variable affinity.

Tarazona *et al* [13] determined nine major and minor elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and thirteen trace elements(Ba, Cr, Cu, Mn, Nb, Ni, Pb, Rb, Sr, V, Y, Zn, and Zr) by X-ray fluorescence spectrometry in Austrian bituminous coals. They established the organic affinities of these trace metals using calculations based on concentration – ash content relation or on the detrital mineralogy. They concluded that detrital and diagenetic minerals are the host for most of the trace elements. They argued that trace concentration in the lightest coal fractions cannot be regarded as bound to organic matter, but is part of the fine grained detrital minerals which are homogeneously distributed in the organic matrix of coal.

Preis *et al* [14] developed a correlation model and related it to the organic and inorganic affinities of trace elements present in Kaffioyra and Longyearbyen coals from Spitsbergen regions in Norway. They found that trace elements in Kaffioyra coals showed a high degree of inorganic association. Zinc, Co, Li, Mn, Ni, Pb and V are bound 100% to mineral matter, while Cd, Cr and Cu are bound 100 % to organic matter. Berrilium only was found to have values in the range of 30% organic and 70 % inorganic In Longyearbyen coals Cr and and V are 100%

bound to inorganic fractions, while Be, Co, Cu, and Ni are bound 100% to the organic fraction. Zinc, Cd, Li, Mn and Pb show variable affinity to both fractions in these coals.

Huggins *et al* [15] determined modes of occurrence of some major and trace metals in an Illinois coal and fractions obtained by several physical separation techniques. They observed that K and Fe were present entirely in inorganic forms. Calcium was present from 80 to 90 % in inorganic form; the remainder was present as bound to carboxyl groups. Chromium and V were present predominantly in inorganic forms, with minor amounts having organic association (5-10 % Cr, 20-30%V). Arsenic and Zn were present almost entirely in inorganic forms distributed among various inorganic minerals.

Our earlier studies [16,17] of extraction of these coal samples with different leachants showed that trace metals like Cu, Zn, Mn, Fe, Mg, K and Na were present both as ion-exchangeable cations (extractable with ammonium acetate) and as part of discrete-mineral particles (extractable with acids). The amounts of ion-exchangeable metals however were quite less compared to their respective amounts present as discrete mineral particles. Our earlier work on Scanning Electron Microscopic studies [18] of virgin coal samples and coal samples after extraction with different leachants, pointed to the existence of homogeneously distributed network of mineral matter in the organic matrix of coal, comprised of micro filamentous crystallites (discrete mineral particles) and as surface coverage (ion-exchangeable cation). Furthermore SEM micrographs of coal samples extracted with ammonium acetate revealed surface disintegration in the form of micro fissures, cracks, crevices and valleys

which indicated the extraction of organically bound elements.

In our earlier studies [19], using float and sink separation for four Pakistani coals, it was observed that Makarwal and Sor-Range coals had the highest amount of ash forming materials in the float fraction, where as in Degari and Shahrigh coal samples, most of the ash forming material were found to be enriched in the sink fraction, this showed that in Makarwal and Sor-Range coal samples, most of the ash forming material might be present in close association with the coal structure. On the other hand, in case of Degari and Shahrigh coal samples, significant amount of their ash forming material might have been present as discrete mineral matter. In the present work the ash of float and sink fractions of the four Pakistani coal samples have been analyzed for some trace metals in continuation to our earlier work in an attempt to know, whether these elements are bound organically or occur as part of the discrete mineral matter.

2. EXPERIMENTAL

2.1 FLOAT AND SINK SEPARATION OF COAL SAMPLES

Representative coal samples obtained through Pakistan Mineral Development Corporation from four coal mines in Pakistan were studied in the present investigation.

Selected coal lumps free from visible lumps of inorganic matter were used for float and sink analysis in order to avoid the mineral matter inclusions due to roofs and floors of coal mines as were present in the representative samples. The coal samples were crushed in a pestle and mortar and were screened through 0.6mm and 0.3mm screens using a vibrating shaking screen. The products which passed through 0.6mm screen and retained on 0.3mm screen were dried at 110 °C and used

for washability studies using media of different specific gravities [19].

2.2 SAMPLE SOLUTION PREPARATION

The various float and sink fractions as well as the whole coal sample were ashed at 750 °C in a muffle furnace for 2-4 hrs and the resulting ash was weighed. The ash from the various fractions were dissolved by digesting with HF and H₂SO₄ in a platinum crucible to volatilize silica and then treated with HCl to solubilize the trace metals present in the ash. The solutions were diluted to 100 cm³ with distilled water and stored in polyethylene bottles for trace metals analysis.

2.3 TRACE METALS DETERMINATION

Trace metals in the sample solutions prepared above, were determined using a Pye Unicam Model SP 191 Atomic Absorption Spectrophotometer. Working sample solutions were prepared by diluting appropriate volumes of the original filtrate with distilled water so as to get reading within the range of working standards.

Standard stock solution for various metals

were prepared by dissolving pure metal or their salts of Analar or chemical reagent grades according to standard procedure of solution preparation for Atomic Absorption Spectrophotometer. Four working standard solutions were prepared for each metal in the concentration range of 1-5 ppm (Cu), 1-5 ppm (Ni), 1-5 ppm (Zn) and 1-5 ppm (Co) by diluting appropriate volume of the stock solution with distilled water. The operational conditions for metal determination by Atomic absorption Spectrophotometer is give in Table 1.

TABLE 1: OPERATIONAL CONDITIONS FOR METAL DETERMINATION

Metal	Flame Used	Slit Width (nm)	Wavelength (nm)	Sensitivity
Cu	Air/Acetylene	0.2	324.75	0.025
Ni	Air/Acetylene	0.2	232.00	0.05
Zn	Air/Acetylene	0.2	213.88	0.009
Co	Air/Acetylene	0.2	240.72	0.06

3. RESULTS AND DISCUSSION

The analysis of four representative Pakistani coal samples obtained from Makarwal, Shahrih, Sor-Range, and Degari coal mines is given in Table 2.

TABLE 2: ANALYSIS OF FOUR REPRESENTATIVE PAKISTANI COAL SAMPLES

Analysis/Sample	Makarwal	Shahrih	Sor-Range	Degari
Moisture(as received) %	4.12	4.67	9.37	8.09
Moisture holding capacity %	6.13	9.00	13.00	12.70
Volatile Combustible Matter V.C.M (as received) %	43.08	42.15	46.13	40.78
V.C. M (Dry, MM free) %	48.22	66.60	54.60	52.30
Ash (Rep. Sample) %	4.12	26.85	5.27	10.95
Ash (Select. Lump sample) %	1.95	13.27	5.37	9.26
Ash (R.O.M.) Sample %	24.00	33.50	13.93	38.67
Mineral Matter (Parr Formula) %	6.55	32.04	6.15	13.94
Fixed Carbon (As Received) %	48.68	26.33	39.23	40.18
Fixed Carbon (Dry MM free) %	53.85	40.29	46.28	50.79
Calorific Value (As Received) (Kcal/kg)	6651	4553	5596	5526
Calorific Value (Moist. MM Free) (kcal/kg)	5328	3075	4477	4596
Total S (Eschka Method) %	3.82	5.53	0.84	3.84
Total S (Bomb Combust. Method) %	3.80	5.48	0.83	3.81
Sulphatic S %	0.14	0.89	0.05	0.15
Pyretic S %	0.02	0.64	0.16	0.34
Organic S %	3.66	4.00	0.63	3.35
Total Cl (Eschka Method) %	0.12	0.24	0.19	0.24
Total Cl (Bomb Combust. Method) %	0.12	0.24	0.20	0.24

V.C.M- Volatile combustible matter, MM free- Mineral matter free, R.O.M.- Run of mine, Parr formula- %MM = 1.08A + 0.55S (MM- Mineral Matter, A- Percentage of Ash in the Sample, S- Percentage of Total Sulfur in the Sample).

The analysis given in Table 2, shows that these coals have low calorific value, high volatile matter, high ash and high sulfur content, and range from lignite to sub bituminous in rank. The ash content of the representative samples, selected lump samples and run of mine (ROM) samples show considerable difference. The ash content of the run of mine samples is appreciably high compared to the representative and selected lump. The various forms of sulfur present in these coals have also been given in Table 2, which indicates that all these coals contain sulfur in the form of pyretic, sulphatic and organic forms. The organic sulfur is present in appreciable amount in all the four coal samples compared to pyretic and sulphatic forms. The concentrations of Co, Cu, Ni, and Zn determined in the selected whole coal lump samples are given in Table 3 and Fig. 1. The world averages reported for these metals by Dai *et al* [6] have also been included in the table for comparison.

TABLE 3: TRACE METALS CONTENTS IN WHOLE COAL OF FOUR PAKISTANI COAL SAMPLES

Coal Sample	%Ash	Co ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
Makarwal Coal	1.95	6	20	10	30
Shahrigh Coal	13.27	10	30	50	60
Sor-Range Coal	5.37	8	20	10	20
Degari Coal	9.62	10	20	40	60
World Average	-----	5.1	16	13	23

The results show that most of the metals have high concentration in the four coal samples compared to their respective values of the world average. The Zn and Ni contents in Shahrigh and Degari coals are high compared to their respective amounts in Makarwal and

Sore-Range coals. The Zn content is appreciably high in all the four coal samples compared to the world average. The Ni content is appreciably high compared to the world average in case of Shahrigh and Degari coals, whereas Makarwal and Sore-range coals have lower values compared to the world average.

Fig.1. Concentration of Trace Elements in Whole Coal

Table 4 and Fig.2 show the float and sink fractions of Makarwal coal at different specific gravities.

Fig.2. Weight Percentage of Float and Sink Fractions in Makarwal Coal at Different Specific Gravities

The results show that float fraction is quite low at the lowest specific gravity (sp.g 1.282), whereas most of coal is present in the sink fraction. The percentage of float fraction has increased with increase in specific gravity of the medium. At the highest specific gravity (sp.g.1.632), the coal is present almost in the float fraction (99.65). The sink fraction is quite negligible.

TABLE 4: TRACE METALS CONTENTS IN FLOAT AND SINK FRACTIONS OF MAKARWAL COAL.

Float/ Sink Fractions	Fractions Wt%	%Ash	Co ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
Float Fraction (Sp.G.1.282)	0.50	---	---	---	---	---
Sink Fraction (Sp.G.1.282)	99.50	2.29	5	15	5	46
Float Fraction (Sp.G.1.365)	52.92	0.96	10	14	9	28
Sink Fraction (Sp.G.1.365)	47.08	3.18	11	28	17	90
Float Fraction (Sp.G.1.385)	69.26	1.21	7	14	14	43
Sink Fraction Sp.G.1.385)	30.74	3.68	19	25	24	107
Float Fraction (Sp.G.1.489)	98.48	1.53	5	13	5	40
Sink Fraction (Sp.G.1.489)	1.52	---	---	---	---	---
Float Fraction (Sp.G.1.632)	99.65	1.83	8	13	5	15
Sink Fraction (Sp.G.1.632)	0.35	---	---	---	---	---

The weight percentage of ash in the float and sink fractions in Makarwal coal at different specific gravities given in Table 4 and illustrated in Fig.3, show that the ash percentage is negligibly small in the float fraction at the lowest specific gravity of 1.282. A gradual increase in the ash percentage in the float fractions can be easily noticed with increase in specific gravity of the medium.

Fig.3. Weight Percentage of Ash in Float and Sink Fractions in Makarwal Coal at Different Specific Gravities

The ash percentage in the sink fractions show an initial increase and then decrease with increase in specific gravity of the medium. The ash percentage in the float fraction is highest at the specific gravity 1.632, whereas in the sink fractions it is highest at the specific gravity 1.385. At the highest specific gravity of 1.632, ash percentage in the sink fraction is almost negligible. The negligibly small percentages of ash in the float fraction at specific gravity 1.282 and the sink fraction at

specific gravity 1.632 is because of their respective negligibly small weight fractions at these specific gravities. These results also indicate that in Makarwal coal, almost all of the ash forming material is closely associated with the organic coaly matter. Discrete mineral particles if present would have been substantially concentrated in the sink fraction at the highest specific gravity.

The concentrations of trace elements in the float and sink fractions at different specific gravities of Makarwal coal are included in Table 4 and illustrated in Fig.4.

Fig.4. Concentration of Trace Elements in Float and Sink Fractions of Makarwal Coal at Different Specific Gravities

The results show that at specific gravities 1.282 and 1.632, almost all metals are present respectively in the sink and float fractions. These are in accordance to their respective float and sink weight fractions (Fig.2) and ash percentage of float and sink fractions (Fig.3) at different specific gravities. Figure 4 clearly

shows that Zn is present in highest concentration in almost all fractions compared to other metals. Increase in concentration of all metals can be noticed both in the float and sink fractions with increase in specific gravity of the medium till specific gravity 1.385. Further increase in specific gravity caused a decrease in their respective concentration. These are in accordance to the results of ash percentage of float and sink fractions at different specific gravities (Fig.3). Almost all the metals show high concentration in the sink fractions at specific gravities 1.3655 and 1.385. High concentration of metals at these specific gravities might be due to the high specific gravity of the coaly matter to which these metals are associated in high concentration, compared to the specific gravity of the coaly matter having less concentration of these metals. The unexpected low values of trace metals in the float fraction in medium of specific gravity 1.632 might be due to retainment of the float-sink liquid medium in the coal fraction which was not completely removed by drying at 110 °C for calculating the percentage of weight fractions.

Table 5 and Fig.5 show the float and sink fractions of Shahrigh coal at different specific gravities.

The results show that float fraction is quite low at the lowest specific gravity (sp.g 1.282), whereas most of the coal is present in the sink fraction at this specific gravity, similar to Makarwal coal. In Shahrigh coal the float fraction at this specific gravity is 10.05 % compared to 0.5 % in Makarwal coal at the same specific gravity. The percentage of float fractions has increased with increase in specific gravity of the medium, whereas the percentage of sink fractions has decreased. At the highest specific gravity (sp.g.1.632), 15.97 % of coal is present in the sink fraction

compared to 0.35 % in case of Makarwal coal, indicating that comparatively high inorganic matter is present as discrete mineral particles which settle down at the highest specific gravity.

Fig.5. Weight Percentage of Float and Sink Fractions in Shahrigh Coal at Different Specific Gravities

The weight percentage of ash in the float and sink fractions at different specific gravities is given in Table 5 and illustrated in Fig.6.

Fig.6. Weight Percentage of Ash in Float and Sink Fractions in Shahrigh Coal at Different Specific Gravities

The ash percentage in the float fractions is almost constant at all the specific gravities in contrast to that in Makarwal coal which shows an increasing trend with increase in specific gravity of the medium. It is to be pointed out that percent ash is significantly high in whole coal and the various fractions, especially the sink fractions in case of Shahrigh coal compared to Makarwal coal. A gradual increase in the ash percentage in the sink fraction can be noticed with increase in specific gravity of the medium. The ash

percentage at the specific gravity 1.489 and 1.632 are quite high compared to Makarwal coals. The results show that in contrast to Makarwal coal, a significant fraction of the inorganic matter in this coal may be present in the form of discrete mineral particles which

settle easily in the liquid medium of high specific gravity. The concentration of trace elements in the float and sink fractions at different specific gravities of Shahrigh coal is included in Table 5 and illustrated in Fig.7.

TABLE 5: TRACE METALS CONTENTS IN FLOAT AND SINK FRACTIONS OF SHAHRIGH COAL.

Float/ Sink Fractions	Fractions Wt%	%Ash	Co (µg/g)	Cu (µg/g)	Ni (µg/g)	Zn (µg/g)
Float Fraction (Sp.G.1.282)	10.05	1.69	11	11	---	6
Sink Fraction (Sp.G.1.282)	89.95	15.58	34	34	30	21
Float Fraction (Sp.G.1.365)	68.26	2.89	---	7	7	7
Sink Fraction (Sp.G.1.365)	31.74	42.90	32	40	79	47
Float Fraction (Sp.G.1.385)	72.11	3.56	7	7	7	7
Sink Fraction (Sp.G.1.385)	27.89	44.60	33	47	92	66
Float Fraction (Sp.G.1.489)	79.71	4.46	---	25	9	19
Sink Fraction (Sp.G.1.489)	20.29	61.05	35	29	115	93
Float Fraction (Sp.G.1.632)	84.03	5.08	6	9	15	12
Sink Fraction (Sp.G.1.632)	15.97	60.80	46	60	125	75

The results show a progressive increase in the Ni and Zn contents in the sink fractions with increase in specific gravity of the medium. The Ni concentration, however is less at the highest specific gravity 1.632 compared to its value at the specific gravity 1.489. Of the four metals, Ni is present in the highest concentration in the sink fractions at the specific gravities 1.365, 1.385, 1.489 and 1.632. The concentrations of all the metals are appreciably high compared to their amounts in Makarwal coal. The comparatively higher trace metal contents at the high specific gravities is in conformity to the higher weight percentage of ash at high specific gravities in this coal (Fig.6). The results also show, that where as Zn is present in the highest concentration in the sink fractions at all the specific gravities in case of Makarwal coal, Ni is present in the highest concentrations in the sink fractions at all the specific gravities in case of Shahrigh coal. High metal contents in the sink fractions especially Ni and Zn indicate that major part of these metals may be present in close association with the inorganic matter in this coal.

Table 6 and Fig.8 show the float and sink fractions of Sore-Range coal at different specific gravities.

Fig.7. Concentration of Trace Elements in Float and Sink Fractions of Shahrigh Coal at Different Specific Gravities

Fig.8. Weight Percentage of Float and Sink Fractions in Sor-Range Coal at Different Specific Gravities

Sore range coal shows behavior similar to Makarwal coal. The float fraction is the lowest at the lowest specific gravity of 1.282, whereas the sink fraction is the lowest at the highest

specific gravity of 1.632. A progressive increase in the float fraction and a decrease in

the sink fraction can be noticed with increase in specific gravity of the medium.

TABLE 6: TRACE METALS CONTENTS IN FLOAT AND SINK FRACTIONS OF SOR-RANGE COAL.

Float/ Sink Fractions	Fractions Wt%	%Ash	Co ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
Float Fraction (Sp.G.1.282)	2.00	---	---	---	---	---
Sink Fraction (Sp.G.1.282)	98.00	5.58	10	26	23	30
Float Fraction (Sp.G.1.365)	23.30	4.19	---	22	---	31
Sink Fraction (Sp.G.1.365)	76.70	6.01	7	32	19	23
Float Fraction (Sp.G.1.385)	43.00	3.65	12	22	12	44
Sink Fraction (Sp.G.1.385)	57.00	6.98	9	26	9	16
Float Fraction (Sp.G.1.489)	97.57	4.10	8	21	8	8
Sink Fraction (Sp.G.1.489)	2.43	---	---	---	---	---
Float Fraction (Sp.G.1.632)	99.40	4.47	10	30	15	23
Sink Fraction (Sp.G.1.632)	0.60	---	---	---	---	---

The weight percentage of ash in the float and sink fractions at different specific gravities is given in Table 6 and illustrated in Fig.9.

Fig.9. Weight Percentage of Ash in Float and Sink Fractions in Sor-Range Coal at Different Specific Gravities

The weight percentage of ash in the float and sink fractions follow a pattern similar to Makarwal Coal. A progressive increase in ash percentage of the float fractions with increase in specific gravity of the medium can be noticed. The ash percentage in the sink fractions shows an increasing trend with increase in specific gravity, till it reaches to its highest value at 1.385. Further increase in specific gravity caused a decrease in the ash percentage.

The negligibly small percentages of ash in the float fraction at specific gravity 1.282 and the sink fraction at specific gravity 1.632 is because of their respective negligibly small weight fractions at these specific gravities as

noticed in Makarwal coal. The ash percentage of the float and sink fractions in Sore-Range coal indicates that substantial amount of the inorganic matter may be closely associated with the organic coaly matter similar to Makarwal coal. Sore-Range coal has significantly low percent ash content in whole coal and in the various float and sink fractions as compared with their respective values in case of Shahrigh coal.

The concentration of trace elements in the float and sink fractions at different specific gravities of Sore-Range coal is included in Table 6 and illustrated in Fig.10.

Fig.10. Concentration of Trace Elements in Float and Sink Fractions of Sor-Range Coal at Different Specific Gravities

The results show that at specific gravities 1.282 and 1.632, almost all metals are present respectively in the sink and float fractions similar to Makarwal coal. The trace metals in

the float fraction at the lowest specific gravity 1.282 and in the sink fraction of the highest specific gravity 1.632 were not detected. In the mid specific gravity of 1.385, all metals are present appreciably in both the float and sink fractions, similar to Makarwal coal. The results also show that in Sore-Range coal Zn is present in the highest concentration compared to other metals. Zinc was also found in highest concentration in most of the fractions in Makarwal coal.

The almost zero values of all the trace metals in the sink fraction at the highest specific gravity 1.632 indicate that in Sore-Range coal almost all the trace metals may be present in close association to the organic structure of coal similar to Makarwal coal.

The float and sink fractions at different specific gravities of Degari coal is given in Table 7 and Fig. 11.

Fig.11. Weight Percentage of Float and Sink Fractions in Degari Coal at Different Specific Gravities

TABLE 7: TRACE METALS CONTENTS IN FLOAT AND SINK FRACTIONS OF DEGARI COAL.

Float/ Sink Fractions	Fractions Wt%	%Ash	Co (µg/g)	Cu (µg/g)	Ni (µg/g)	Zn (µg/g)
Float Fraction (Sp.G.1.282)	0.51	---	---	---	---	---
Sink Fraction (Sp.G.1.282)	99.49	8.21	5	15	15	29
Float Fraction (Sp.G.1.365)	66.82	3.33	---	15	8	29
Sink Fraction (Sp.G.1.365)	33.18	23.25	38	28	46	77
Float Fraction (Sp.G.1.385)	74.20	3.53	---	10	13	14
Sink Fraction (Sp.G.1.385)	25.80	31.03	18	87	46	148
Float Fraction (Sp.G.1.489)	86.92	3.74	---	14	6	14
Sink Fraction (Sp.G.1.489)	13.08	50.23	125	21	248	186
Float Fraction (Sp.G.1.632)	88.80	4.49	6	39	8	11
Sink Fraction (Sp.G.1.632)	11.20	60.31	140	832	273	898

An increasing trend in the weight percentage of float fraction and a decreasing trend of the sink fraction can be noticed similar to other coals.

The weight percentage of ash in the float and sink fractions at different specific gravities is given in Table 7 and illustrated in Fig.12. The ash percentage in the whole coal and the various float and sink fractions is significantly high compared to their respective values in case of Makarwal and Sore-Range coals and almost similar to Sharigh coal. An increasing trend in the percent ash in the sink fraction with increase in specific gravity of the medium can be seen. The trend is similar to that observed in Sharigh coal. A considerable

enrichment of the ash forming inorganic matter has occurred in the sink fractions at high specific gravities.

Fig.12. Weight Percentage of Ash in Float and Sink Fractions in Degari Coal at Different Specific Gravities

This indicates that similar to Sharigh coal a significant part of the inorganic matter might

be present as discrete mineral matter, which can easily be separated as sink fraction in medium of high specific gravities.

The concentrations of trace elements in the float and sink fractions at different specific gravities of Degari coal are included in Table 7 and illustrated in Fig.13.

Fig.13. Concentration of Trace Elements in Float and Sink Fractions of Degari Coal at Different Specific Gravities

An increase in concentration of trace metals has occurred in the sink fractions with increase in specific gravity of the medium, similar to Shahrigh coal. The concentration of Cu and Zn in Degari coal is quite large in sink fractions at the highest specific gravity 1.632. High concentration of trace metals especially Cu and Zinc at higher specific gravities indicates that most part of these elements might be present as part of discrete mineral particles, which can easily be separated from organic coaly matter in medium of high specific gravities.

Figure 14 shows the weight percentage of float fractions at different specific gravities in different coal samples. An increasing trend can be noticed in all the coal samples with increase in specific gravity of the medium. The float fractions are highest in the two higher specific gravities. Figure 15 shows weight percentage of ash in float fractions in

medium of different specific gravities of the four coal samples.

Fig.14. Weight Percentage of Float Fractions in Different Coal Samples at Different Specific Gravities

Fig.15. Weight Percentage of Ash in Float Fractions in Different Coal Samples at Different Specific Gravities

An increase can be noticed in the percent ash with increase in specific gravity of the medium.

The concentration of trace elements in the float fractions of all the coal samples at different specific gravities is shown in Fig.16. The figure shows that concentration of trace metals especially Zn was appreciably high in the float fractions at specific gravities 1.385 and 1.489 in case of Makarwal and Sore-Range coal samples.

Other coals show variable concentration of trace metals at different specific gravities in the float fractions.

Fig.16. Concentration of Trace Elements in Float Fractions of Coal Samples

Figure 17 shows weight percentage of sink fractions of different coals at different specific gravities. A decreasing trend can be noticed in the weight percentages of sink fractions of most of the coals with increase in specific gravity of the medium as discussed earlier.

Fig.17. Weight Percentage of Sink Fractions in Different Coal Samples at Different Specific Gravities

Figure 18 shows percentage of ash in the sink fractions of the four coal samples at different specific gravities. The increase in ash percentage with increase in specific gravity is quite significant in case of Sharigh and Degari coals compared to the other two coal samples.

Fig.18. Weight Percentage of Ash in Sink Fractions in Different Coal Samples at Different Specific Gravities

As discussed earlier, high ash content in the sink fractions of these coals at the higher specific gravities indicate that significant part of the ash forming matter may be present in association to the inorganic matter in coal which can easily be separated in medium of high specific gravities.

Figure 19 shows the trace metal content in sink fractions of all the four coal samples at different specific gravities. The figure clearly shows that significant enrichment of trace metals has occurred in the sink fractions of

Shahrigh and Degari coal samples with increase in specific gravity of the medium. Most of the trace metal contents are highest at the highest specific gravity 1.632. Previous studies based on float and sink analysis [1-18] indicates different degree of organic and inorganic association of various trace metals in case of different coals. An element having high organic association in one coal sample might have high inorganic association in another coal. Even though float and sink separation is generally being used for

determining the organic and inorganic association of trace elements in coal, trace elements in the float fraction may not be indicative of their true organic association in the coal structure. Enrichment of trace element might also be due to the presence of fine grained mineral particles embedded in the organic coaly matrix which are carried in the float fraction due to the overall low specific gravity of the coal particles containing these fine sized mineral grains.

Fig.19. Concentration of Trace Elements in Sink Fractions of Coal Samples

4. CONCLUSION

Four Pakistani coal samples were separated in to float and sink fractions using media of different specific gravities. Trace elements Co, Cu, Ni and Zn were determined in the whole coal and the various float and sink fractions. Following is a summary of our findings.

1. In Makarwal and Sore-Range coals, major part of Co, Cu, Ni and Zn may be present in close association to the organic coaly matter as ion-exchangeable ions, adsorbed species , organometallic complexes or as submicron size mineral particles embedded in the coal structure so intimately which are difficult to be separated by the float and sink method.

2. In Shahrigh coal, Zn and Ni and in Degari coal, Zn and Cu may be present predominantly in inorganic forms which can easily be separated by float and sink method in medium of high specific gravity. Other trace metals in these coals might have variable association.

A detailed investigation is needed about the mode of occurrence of trace metals in these coals using modern instrumental techniques such as Instrumental Neutron Activation Analysis (INAA), Inductively Coupled Mass Spectrometry (ICP-MS) X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), and Scanning Transmission Electron Microscopy (STEM).

ACKNOWLEDGEMENT

The author is grateful to Mr.Kamran Usmani, secretary, Department of Chemical Engineering Technology and Mr Haider Ali, Department of Instructional Support Services, Yanbu Industrial College for their help in writing this manuscript.

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دراسة خاصة الفصل بالغسيل لأربع عينات فحم من مناطق مختلفة في الباكستان باستخدام تقنية التعويم للحصول على العائم (الخفيف) والجزء الغاطس (الثقيل)

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الملخص:

هذه الدراسة أجريت على عينات من الفحم من مناطق مختلفة في الباكستان حيث تم فصلها إلى جزئين، جزء خفيف عائم وجزء ثقيل غاطس، باستخدام مواد تعويم ذات كثافة نوعية مختلفة . بعد حرق عينات الفحم والأجزاء الناتجة عن عمليات التعويم (الخفيف والثقيل) في فرن حراري على درجة 750م للحصول على الرماد والذي تم تحليله بطريقة الإمتصاص الذري الطيفي لتحديد نسب الكوبالت والنحاس والنيكل والزنك قبل وبعد عملية التعويم .

لقد بينت النتائج أن تراكيز هذه المعادن كانت قليلة في الجزء الثقيل في عينات الفحم من مناطق ماكاروال وسورينج ولكن وجد أن تراكيز المعادن أعلى في الجزء الثقيل لعينات الفحم التي تم أخذها من مناطق ديغاري وشاهري . لقد تم شرح النتائج بالإعتماد على درجة ارتباط هذه المعادن بالمواد العضوية الموجودة في الفحم حيث عزي تناقص هذه المعادن في الجزء الثقيل للعينات المأخوذة من ماكاروال وسورينج إلى قوة ارتباط هذه المعادن بالبناء العضوي للفحم مما يؤدي إلى صعوبة فصلها بطرق التعويم العادية. وفي حالة عينات الفحم من مناطق ديغاري وشاهري فمن الممكن أن تكون المعادن لها رابطة ضعيفة في مركبات الفحم العضوية بحيث يسهل فصلها بطرق التعويم الرغوي.