

Beneficiation Study on Low-Grade Graphite Ore of Shounter Valley, Azad Kashmir, Pakistan

Muhammad Arif Bhatti, Kamran Raza Kazmi, Samreen Zahra*, Ansar Mehmood and Rashid Mehmood
Mineral Processing Research Centre, PCSIR Laboratories Complex, Ferozepur Road, Lahore-54600, Pakistan.
samreenzahra68@hotmail.com*

(Received on 2nd August 2017, accepted in revised form 12th July 2019)

Summary: A low-grade graphite ore originating from Kael area, Shounter Valley, Azad Kashmir, assaying 8.90% graphite content was upgraded by froth flotation technique to produce a commercial grade graphite concentrate. Mineral phases present in the ore were identified by using X-ray diffraction (XRD) technique. The variables of flotation process such as particle size of the feed, pH of the pulp, % solids of the pulp, speed of impeller, type and quantity of collecting and frothing agents, conditioning time and froth collecting time were optimized to get maximum grade and recovery of graphite mineral. The pH of the pulp was adjusted with sodium carbonate. Kerosene oil was used as collector while pine oil as frother respectively. Sodium silicate was employed as depressant. The grade of the final graphite concentrate produced was 85.80% C with overall recovery of 86.00%. Its surface morphology was studied using SEM-EDX technique while grain size by laser particle size analyzer.

Key words: Low-grade ore; Graphite; Beneficiation; Froth flotation; Grade; Recovery.

Introduction

Graphite is a well known mineral having distinct physical properties like refractoriness, lubricating nature, high thermal stability and conductivity that make it quite important for various industrial applications. It is predominantly used in foundry, refractory, crucibles and electrodes. Other applications include pencils, explosives, electrotyping, rubber, scale inhibitors, lubricants and paints etc. Graphite occurs in nature as flaky aggregates and fine grains distributed in schistose rocks and also in veins [1-3]. It is generally produced as a consequence of metamorphism of sediments containing substantial quantities of organic matter. Both flaky as well as amorphous forms of graphite are produced depending upon the grain size of sediments [4]. In addition to size and distribution of grains, tonnage and grade of the ore bodies play a vital role in the economic exploitation of graphite deposits [5].

World's largest reserves of flaky or crystalline graphite are available in Austria, Brazil, Canada, China, Germany and Madagascar whereas huge deposits of amorphous graphite occur in China, Europe, Mexico and United States. During the previous years, continuous advancement of economic conditions all over the world has greatly influenced the end-use of graphite and hence increased its demand. In the year 2012, China was at the top with 67% of the entire world production of graphite, followed by India, Brazil, North Korea, Canada, and Russia, in descending order [6]. In 2013, the

production of graphite increased in China, Madagascar and Sri Lanka maintained its position as the leading producer [7].

In Pakistan, massive deposits of low-grade graphite ore containing 10-20% graphitic carbon occur in Khyber Pakhtoon Khawa province and Azad Kashmir. But unfortunately, the local requirement of foundry grade graphite having 75-85% graphitic carbon is met through import. Annual import of graphite is 5000-6000 tons that costs around 60 million rupees, which can be easily substituted by the production of good quality product from naturally occurring graphite of lower purity. This low-grade natural graphite essentially needs beneficiation for the economic development of high-grade graphite concentrates [2, 8, 9]. Most of the previous scientists have applied froth flotation and gravity concentration for upgrading graphite. In fact, the selection of process strongly depends upon the presence of associated gangue minerals. The principal mechanism applied all over the world for the concentration of low grade graphite ore is froth flotation because of its natural hydrophobicity [4, 10, 11]. Along with froth flotation, chemical treatment like acid leaching is also considered to be essential since, it is difficult to produce high purity graphite only by mechanical processing techniques [12]. Researchers also employed alkali digestion prior to froth flotation followed by acid leaching for attaining 98% purity of graphite [13]. In froth flotation of graphite ores, usually diesel and kerosene are used as

*To whom all correspondence should be addressed.

collectors whereas pine oil, methyl isobutyl carbinol, eucalyptus oil and ethyl alcohol have been employed as frothers [4]. Abdel-Rahiem *et al.* applied flotation process both in conventional flotation cell as well as in column flotation cell for the up-gradation of graphite ore using kerosene as collector [14]. Joni and co-workers used diesel and pine oil as collector and frother respectively and obtained a product of 91% purity [15]. Recently, Vasumathi *et al.* developed an environment friendly single reagent Sokem 705C as a replacement for diesel-frother system and found it more efficient and economically feasible for the flotation of low grade graphite ore [4].

Present paper describes the results of bench scale beneficiation study of graphite ore of Kael area, Shounter valley, Azad Kashmir. The representative sample of ore containing 8.90% graphitic carbon was beneficiated by froth flotation technique and experiments were carried out in Mineral Processing Laboratory to optimize the process parameters that influence the flotation of graphite mineral in order to obtain an industrial grade graphite concentrate.

Experimental

Sample preparation

A bulk sample, weighing about 210 kg, of graphite ore of Kael area, Shounter valley of Azad Kashmir was supplied by Pak-Kashmir Mineral Resources (Pvt.) Ltd., Islamabad. The ore was subjected to primary crushing using laboratory jaw crusher followed by secondary crushing using roll crusher to reduce the size. A representative sample of ore was prepared through coning-quartering and riffing of crushed ore. It was ground to pass through 200 mesh sieve for chemical evaluation and XRD analysis. The remaining portion of crushed ore was packed in plastic bags of one Kg for beneficiation tests.

Chemical analysis

The chemical analysis of the representative ore sample was carried out by conventional as well as instrumental techniques. The carbon content of the ore sample was estimated by using ASTM C709 standard procedure [14]. Moisture, SiO₂, and Al₂O₃ were determined gravimetrically while Fe₂O₃ was found by titration method. CaO and MgO were estimated volumetrically whereas Na₂O and K₂O were analyzed using flame photometer (Jenway PFP-7). The beneficiation products were also analyzed

using the same techniques. The chemical analysis of the representative ore sample is given in Table-1.

Table-1: Chemical analysis of head sample of graphite ore.

Constituents	Percentage (%)
Moisture	0.16
Graphitic Carbon	8.93
SiO ₂	47.90
Al ₂ O ₃	6.53
Fe ₂ O ₃	2.89
CaO	16.79
MgO	10.60
Na ₂ O	2.33
K ₂ O	0.52

X-ray diffraction analysis

In order to identify the minerals present in the ore, the representative ore sample was characterized by Bruker X-ray diffractometer (D8 Advance) using monochromatised CuK_α1 radiation having wavelength of 1.5406Å. X-ray diffractogram (XRD) is shown in Fig. 1. All the peaks were matched using the search-match programme provided with the X-ray diffractometer. The scan parameters are given in Table-2 whereas 2 theta, d-value, relative intensity and the minerals identified are presented in Table-3 respectively.

Table-2: Scan parameters.

Parameter	Description
Scan Axis	Gonio
Start Position [°2Th.]	15.00
End Position [°2Th.]	70.00
Step Size [°2Th.]	0.05
Scan Step Time [s]	2.00
Scan Type	Continuous
Offset [°2Th.]	0.0000
Divergence Slit Type	Fixed
Divergence Slit Size [°]	0.6000
Specimen Length [mm]	10.00
Receiving Slit Size [mm]	0.1000
Measurement Temperature [°C]	25.00
Anode Material	Cu
K-Alpha1 [Å]	1.54060
K-Alpha2 [Å]	1.54439
K-Beta [Å]	1.39225
K-A2 / K-A1 Ratio	0.50000
Generator Settings	40 mA, 40 kV
Goniometer Radius [mm]	217.50
Dist. Focus-Diverg. Slit [mm]	91.00
Incident Beam Monochromator	No
Spinning	No

Preparation of flotation feed

Flotation feeds of different grind sizes were prepared by subjecting the ore to wet grinding in a ball mill with 1:1 solid to liquid ratio.

Table-3: XRD analysis of graphite ore of Kael area, Shouner Valley, Azad Kashmir.

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
19.7647	166.98	0.3936	4.49195	0.45	0.4723	Muscovite
21.0578	170.62	0.1476	4.21893	0.46	0.1771	Quartz
21.9888	1147.56	0.1476	4.04237	3.09	0.1771	Albite
22.9471	223.17	0.1476	3.87567	0.60	0.1771	Calcite/ Albite
23.9243	407.24	0.1476	3.71954	1.10	0.1771	Albite
26.5496	37173.64	0.1968	3.35740	100.00	0.2362	Graphite/ Quartz/ Muscovite
27.5611	1951.51	0.1476	3.23643	5.25	0.1771	Albite
28.5245	2224.55	0.1476	3.12928	5.98	0.1771	Albite
29.8279	3843.16	0.1476	2.99545	10.34	0.1771	Calcite
30.2744	1686.94	0.1968	2.95227	4.54	0.2362	Magnetite
30.8696	1680.81	0.1476	2.89670	4.52	0.1771	Dolomite
31.9077	514.06	0.1476	2.80478	1.38	0.1771	Siderite
33.0882	635.14	0.1476	2.70736	1.71	0.1771	Hematite/ Pyrite
34.9472	2850.85	0.1476	2.56749	7.67	0.1771	Muscovite
35.5682	1983.79	0.2460	2.52408	5.34	0.2952	Magnetite/ Hematite/ Albite
37.6248	96.49	0.2952	2.39070	0.26	0.3542	Pyrite
39.0659	846.00	0.1476	2.30577	2.28	0.1771	Quartz
40.0414	227.07	0.1476	2.25182	0.61	0.1771	Calcite
40.6885	266.37	0.1476	2.21749	0.72	0.1771	Pyrite/ Hematite
41.8877	1737.66	0.1968	2.15674	4.67	0.2362	Dolomite
42.3475	628.15	0.1968	2.13438	1.69	0.2362	Muscovite
42.9194	429.71	0.1476	2.10725	1.16	0.1771	Graphite/ Calcite/ Magnetite
44.3531	2374.33	0.1968	2.04241	6.39	0.2362	Graphite/ Dolomite
45.0243	840.13	0.2952	2.01351	2.26	0.3542	Muscovite
46.0100	415.32	0.1968	1.97264	1.12	0.2362	Graphite
48.8781	105.55	0.2952	1.86339	0.28	0.3542	Calcite
49.6721	444.61	0.1968	1.83545	1.20	0.2362	Quartz/ Hematite
50.7562	303.86	0.1968	1.79876	0.82	0.2362	Dolomite
51.4180	299.80	0.1476	1.77716	0.81	0.1771	Dolomite
52.1069	610.86	0.2460	1.75527	1.64	0.2952	Siderite
54.6840	1744.32	0.1968	1.67849	4.69	0.2362	Graphite/Hematite
56.5789	1047.92	0.2460	1.62669	2.82	0.2952	Pyrite/Graphite/Magnetite
58.1183	350.91	0.1476	1.58722	0.94	0.1771	Calcite
59.5725	393.62	0.2460	1.55190	1.06	0.2952	Quartz
60.6251	229.48	0.3936	1.52745	0.62	0.4723	Graphite
61.7627	265.17	0.2952	1.50202	0.71	0.3542	Muscovite/ Hematite
64.6767	409.85	0.1476	1.44121	1.10	0.1771	Magnetite/ Hematite
66.2672	1905.36	0.2400	1.40927	5.13	0.2880	Dolomite

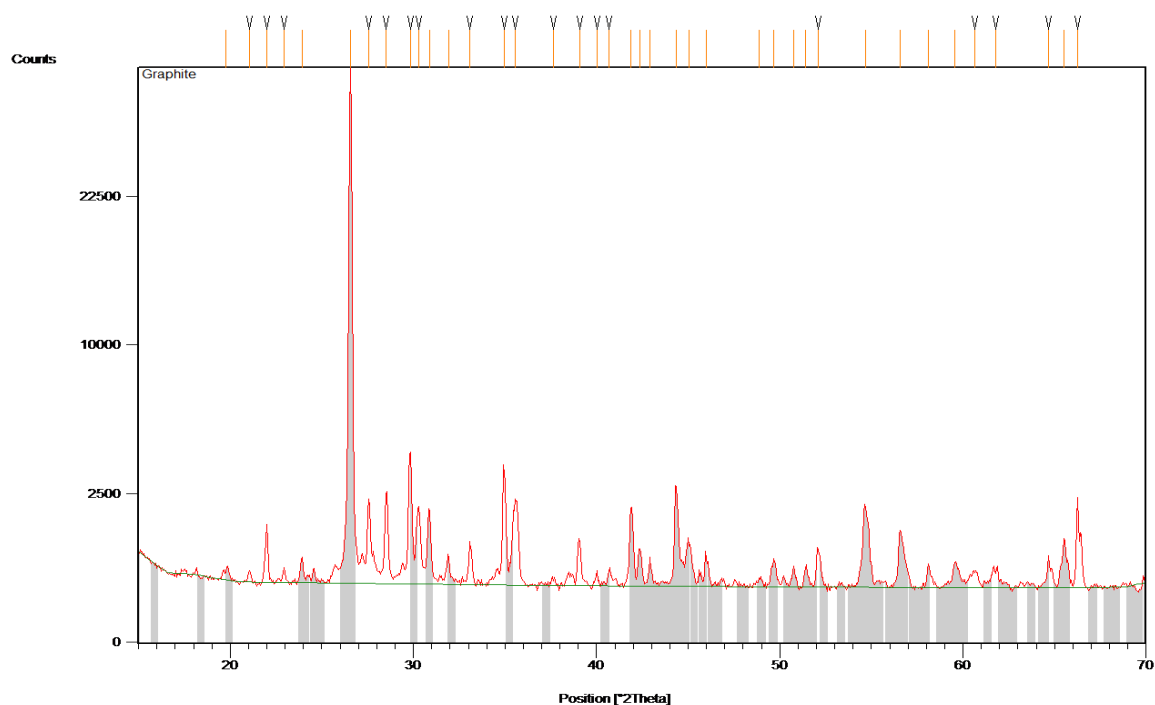


Fig. 1: X-ray diffractogram of graphite ore of Shouner Valley, Azad Kashmir.

Flotation tests

Flotation tests were carried out in a Denver D-12 flotation machine. A series of experiments comprising of roughing, cleaning and re-cleaning flotation were performed by varying flotation parameters i.e. grind size (70-90% passing 100 mesh), pH (7.5-10), pulp density (25-40% solids), quantities of collector (1.0-2.5L/ton), frother (0.01-0.04Kg/ton) and depressant (0.05-0.20Kg/ton), conditioning time (3-6min.) and flotation time (5-15min.). The rougher concentrate obtained was subjected to regrinding prior to two stages of cleaning. Another flotation test was performed to check the effect of re-circulating the re-cleaner tailings to the rougher flotation at optimized conditions. Flow-sheet developed for the overall flotation process is shown in Fig. 2.

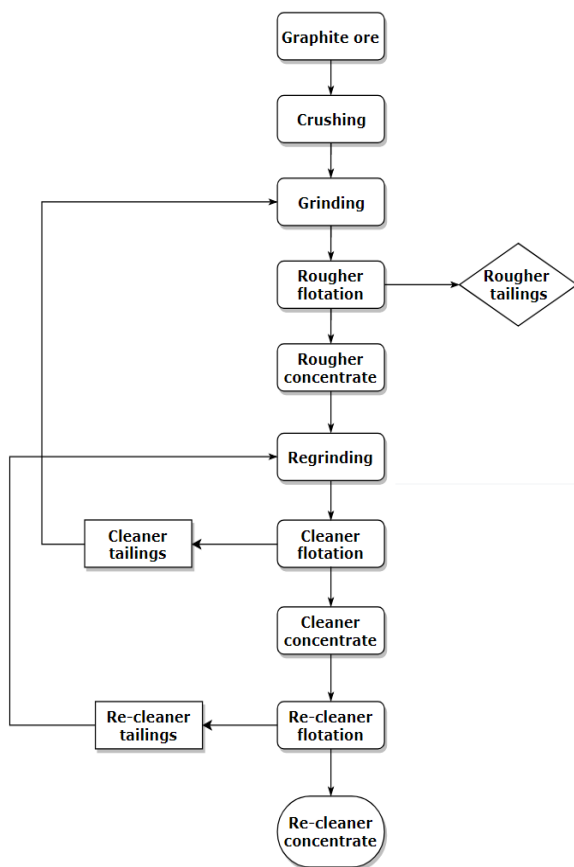


Fig. 2: Flow-sheet for the beneficiation of graphite ore of Shounter Valley, Azad Kashmir.

SEM-EDX analysis

SEM-EDX analysis of the final graphite concentrate was carried out by Scanning Electron Microscopy (S-3700N, Hitachi, Japan).

Particle size analysis

The particle size analysis of final graphite concentrate was determined using Laser Particle Size Analyzer (Bettersizer S2-E, China) at obscuration of 29.51%.

Results and Discussion

Chemical analysis

Chemical analysis of the representative ore sample (Table-1) shows that the graphitic carbon content in the provided sample is 8.90%. Although the obtained grade of ore is low but it is sufficient to exploit it on commercial scale. It is evident from the chemical analysis results that the major impurity is SiO_2 (47.90%) followed by CaO (16.79%), MgO (10.60%) and Al_2O_3 (6.53%). The other impurities found in relatively low content were Fe_2O_3 , Na_2O and K_2O .

X-ray diffraction analysis of graphite ore

The X-ray diffractogram of the graphite ore (Fig.1) shows that the peaks at d values 3.35, 2.04 and 1.67 correspond to the presence of crystalline graphite. The major peak at 2θ of 26° having d-spacing value of 3.35 is the characteristic peak of graphite which is in close agreement with the previous work [15]. As is evident by the chemical analysis that there is a possibility of significant quantities of non-graphite minerals like quartz and feldspar but their corresponding peaks appear at similar positions as crystalline graphite therefore, it can be suggested that they might be overlapped by that of crystalline graphite. Other non-graphite minerals identified were dolomite, calcite, siderite, muscovite, albite, hematite, magnetite and pyrite.

Effect of flotation parameters

It has been inferred by the previous scientists that the beneficiation is usually carried out by size reduction followed by flotation involving multiple stages depending upon the type of ore [17]. A series of rougher flotation tests were therefore carried out on laboratory scale to investigate the effect of parameters i.e. grind size, pH, pulp density, reagents like collector, frother and depressant, conditioning as well as flotation time that influence the grade and recovery of the product.

Effect of grind size

The effect of grind size on the grade and recovery of graphite was studied and results are presented in Table-4. In a series of flotation tests, the various grind sizes of graphite ore ranging from 70 to 100% passing through 100 mesh size were employed while other parameters were kept constant. It is apparent from the results (Table-4) that the grade and recovery of the rougher concentrate improves gradually up to the grind size of 90% passing through 100 mesh. Further reduction in the size leads to an insignificant increase in grade from 23.72 to 24.05% C but significant decrease in recovery of the concentrate from 91.67 to 88.92%. This may be due to the fact that excessive grinding although liberates the fine graphite grains which increase the grade but it also produces more slimes which reduce the recovery. Therefore, the feed size of 90% passing 100 mesh was chosen as optimum and selected for the next series of tests.

Table-4: Effect of grind size on grade and recovery of rougher graphite concentrate.

Grind Size (% - 100 mesh)	Weight %	Grade % (Graphitic Carbon)	Recovery %
70	40.17	19.06	85.74
80	37.06	22.04	91.48
90	34.51	23.72	91.67
100	33.02	24.05	88.92

Effect of pH

One of the most important factors that significantly affect the flotation process is pH of pulp during conditioning. The pH of pulp was adjusted with the addition of soda ash (Na_2CO_3). A number of experiments were carried out at various pH values ranging from natural pH of pulp to 10, keeping all other parameters constant and results obtained are given in Table-5. It can be seen from these results that with the rise in pH up to 9, a gradual increase in both the grade and recovery of product occurs but at higher pH values it starts decreasing probably due to less stability of bond between collector and mineral. However, the maximum grade (23.86% C) and recovery (91.96%) were obtained at pH 9. This indicates that at pH 9, the collector-mineral bond is more stable leading to maximum recovery of graphite. Therefore, the optimum pH was 9 and was applied for further experiments.

Table-5: Effect of pH on grade and recovery of rougher graphite concentrate.

pH of Pulp	Weight %	Grade % (Graphitic Carbon)	Recovery %
Natural	36.67	20.85	85.62
8.0	37.85	21.24	90.02
9.0	34.42	23.86	91.96
10.0	35.60	22.95	91.50

Effect of pulp density

Flotation experiments were carried out to study the effect of pulp density on the grade and recovery of graphite and results are shown in Table-6. The slurry was conditioned at 40, 35, 30 and 25 percent solids whereas other process parameters were kept constant. The results indicate that as the pulp density is reduced from 40% to 30% solids, a slight increase in the grade of graphite concentrate occurs that becomes almost stable at 25% solids. Similarly, a trivial increase in recovery of the product can be seen from 40% to 35% solids that attains stability at 30% solids. However, it decreases significantly as the pulp density is reduced to 25% solids. This may be due to the reason that a higher pulp density produced thick froth layer which is difficult to wash and hinders the proper draining of entrapped gangue particles. Hence, 30% solids were found to be the most favorable pulp density with the highest grade (24.26% C) and recovery (92.05%) of graphite.

Table-6: Effect of pulp density on grade and recovery of rougher graphite concentrate.

Pulp Density (% solids)	Weight %	Grade % (Graphitic Carbon)	Recovery %
40	39.24	20.55	90.31
35	34.34	23.67	91.02
30	33.88	24.26	92.05
25	31.26	24.60	86.12

Effect of collector

Effect of kerosene oil as collector on the grade and recovery of graphite was investigated by varying the dosage of kerosene oil from 1.0 to 2.5 L/ton. Table-7 shows that a gradual improvement in the grade of the product occurs as the dosage of the collector increases from 1.0 to 2.0 L/ton of collector but decreases slightly when 2.5 L/ton of collector is added to the flotation slurry. On the other hand, an appreciable increase in the recovery of the product occurs as the dosage of the collector increases from 1.0 to 2.0 L/ton of collector and finally decreases significantly at 2.5 L/ton of collector dosage due to "over oiling effect" [16]. Hence 2.0 L/ton of kerosene oil was found to be appropriate with 24.37% grade and 92.28% recovery respectively.

Table-7: Effect of collector on grade and recovery of rougher graphite concentrate.

Collector (L/Ton)	Weight %	Grade % (Graphitic Carbon)	Recovery %
1.0	34.54	19.50	75.42
1.5	35.07	23.10	90.73
2.0	33.81	24.37	92.28
2.5	33.46	24.30	91.06

Effect of frother

A series of flotation tests were carried out using pine oil as frother. Various quantities of frother ranging from 0.01-0.04 Kg/ton were employed and its effect on the grade and recovery of graphite concentrate was studied. Results of these experiments are presented in Table-8. It can be seen that no considerable change in the grade of the product appears with the variation in the dose of frother while a gradual increase in the recovery can be seen as the dosage increases from 0.01 to 0.03 Kg/ton. It is evident from these results that 0.03 Kg/ton of pine oil is sufficient to yield a maximum recovery of graphite (92.47%). Moreover, keeping in view the natural floatability of graphite [18] it can be inferred that small quantity of frother is enough for its flotation.

Table-8: Effect of frother on grade and recovery of rougher graphite concentrate.

Frother (Kg/Ton)	Weight %	Grade % (Graphitic Carbon)	Recovery %
0.01	34.07	23.39	89.23
0.02	33.87	24.18	91.72
0.03	33.62	24.56	92.47
0.04	33.52	24.56	92.18

Effect of depressant

Sodium silicate is generally employed as depressant since it can efficiently depress the gangue minerals like quartz and silicates in the flotation medium. The influence of quantity of sodium silicate was therefore investigated. Table-9 shows the results at 0.05, 0.10, 0.15 and 0.20 Kg/ton of sodium silicate added to the flotation medium. It is obvious from these results that highest grade and recovery of graphite concentrate were obtained at 0.15 Kg/ton of the depressant that tend to decrease as the quantity of depressant increases. This effect may be due to the reason that proportionate amount of sodium silicate depresses the gangue minerals efficiently but excessive amount decreases the recovery due to an over coating of some middling particles. Hence, 0.15 Kg/ton of the depressant was the most favorable with 25.16% grade of concentrate and 92.97% recovery respectively.

Table-9: Effect of depressant on grade and recovery of rougher graphite concentrate.

Depressant (Kg/Ton)	Weight %	Grade % (Graphitic Carbon)	Recovery %
0.05	35.80	22.65	90.81
0.10	33.97	24.38	92.75
0.15	32.99	25.16	92.97
0.20	32.03	24.95	89.50

Effect of conditioning time

The conditioning time was varied from 3-6 minutes and its effect on the grade and recovery of the product was investigated. It can be seen from the results given in Table-10 that a conditioning time of 5 minutes is sufficient for an optimum contact of the reagents with the mineral particles for maximum grade (25.56%) and recovery (93.08%) of the product. It can be observed from the results that prolonged conditioning time results in lower grade and recovery.

Table-10: Effect of conditioning time on grade and recovery of rougher graphite concentrate

Conditioning Time (minutes)	Weight %	Grade % (Graphitic carbon)	Recovery %
3	31.71	24.12	85.64
4	32.73	25.38	93.02
5	32.52	25.56	93.08
6	33.30	24.86	92.70

Effect of flotation time

Table-11 shows the variation in flotation time and its influence on the grade and recovery of graphite concentrate. It appears that grade of the concentrate remains almost constant as the time increases from 5 to 15 minutes. However, slight change in the recovery can be observed that attains a maximum of 93.17% at flotation time of 10 minutes that was found to be the optimum time for carrying out flotation process.

Table-11: Effect of flotation time on grade and recovery of rougher graphite concentrate.

Flotation Time (minutes)	Weight %	Grade % (Graphitic carbon)	Recovery %
5	32.14	25.07	90.21
10	32.30	25.76	93.17
15	32.23	25.03	90.35

Effect of cleanings

The optimum flotation conditions established as a result of rougher flotation tests were 90% passing 100 mesh grind size, 9 pH, 30% pulp density, 2.0 L/ton of kerosene oil as collector, 0.03 Kg/ton of pine oil as frother, 0.15 Kg/ton of sodium silicate as depressant, 5 minutes conditioning time and 10 minutes flotation time. The rougher concentrate with 25.76% grade and 93.17% recovery respectively was obtained at optimum conditions. It was then subjected to regrinding up to 100% passing 100 mesh size, followed by cleaner and re-cleaner flotation at appropriate conditions. Tailings of the cleaner and re-cleaner flotation were re-circulated to the flotation feed. The metallurgical balance of typical test performed at optimum conditions is

presented in Table-12. It is important to note that regrinding of the rougher concentrate before the two cleaning operations and re-circulating of cleaner and re-cleaner tailings to flotation feed has ensured a final concentrate grade of 85.80% with 86.00% recovery.

Table-12: Metallurgical balance of a typical lock cycle flotation test of graphite.

Products of Flotation	Weight %	Grade % (Graphitic Carbon)	Recovery %
Recleaner Concentrate	8.95	85.80	86.00
Recleaner Tailings (Cleaner Concentrate)	2.35 (11.30)	13.83 (70.84)	3.64 (89.64)
Cleaner Tailings	21.00	1.50	3.53
(Rougher Concentrate)	(32.30)	(25.76)	(93.17)
Rougher Tailings	67.70	0.90	6.83
Calculated Head Sample	100.00	8.93	100.00

Chemical analysis of the final concentrate

Chemical analysis of the final concentrate given in Table-13 shows that obtained concentrate match with the requirements of foundry grade graphite concentrate and is suitable for the foundry facing purpose and crucible making. However, further removal of contaminants such as silica, iron oxide, aluminum oxide, calcium oxide, magnesium oxide by chemical processing (leaching processes) can make it suitable for wide range of industrial application such as pencil making, electrodes, graphite base lubricant and graphite blocks. The dried concentrate is free of flotation reagents.

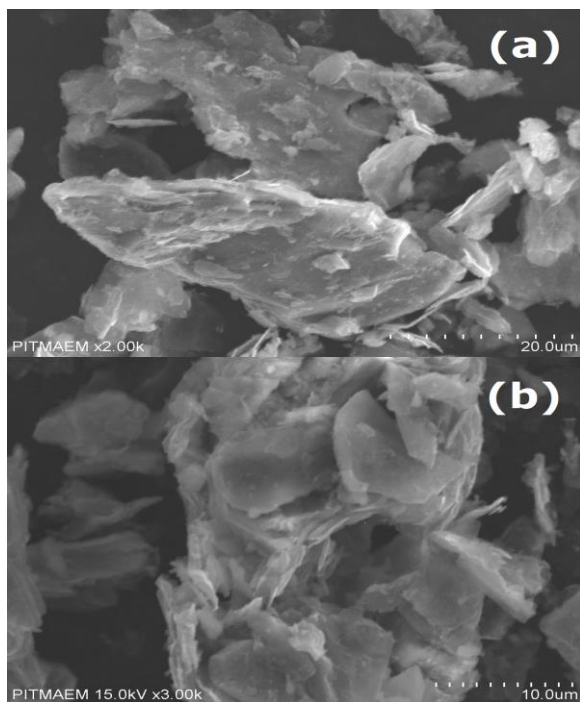


Fig. 3: SEM micrographs of graphite concentrate (a) 2000x magnification, (b) 3000x magnification.

Table-13: Chemical analysis of final graphite concentrate.

Constituents	Percentage (%)
Graphitic Carbon	85.80
SiO ₂	6.31
Al ₂ O ₃	1.02
Fe ₂ O ₃	2.11
CaO	3.51
MgO	0.26
Na ₂ O	0.53
K ₂ O	0.05

SEM-EDX analysis of graphite concentrate

The surface morphology of the graphite concentrate was studied using Scanning Electron Microscopy at 2000x and 3000x magnifications and elemental analysis was carried out using energy dispersive X-ray analysis (EDX) technique. SEM micrographs presented in Fig. 3 (a & b) show the morphology of graphite concentrate. These figures depicts that the flakes of various sizes in micrometers overlap to form irregular multilayered structures similar as observed by the previous scientists [19]. The EDX spectrum shown in Fig. 4 elucidates the presence of carbon as the major component of the product however, other elements like oxygen, aluminum, silicon and iron can be seen in lower quantities; sulphur being present in traces. The weight percent of these elements is shown in Table-14. These results confirm the presence of aluminum oxide, silica and iron oxide as major impurities in the product.

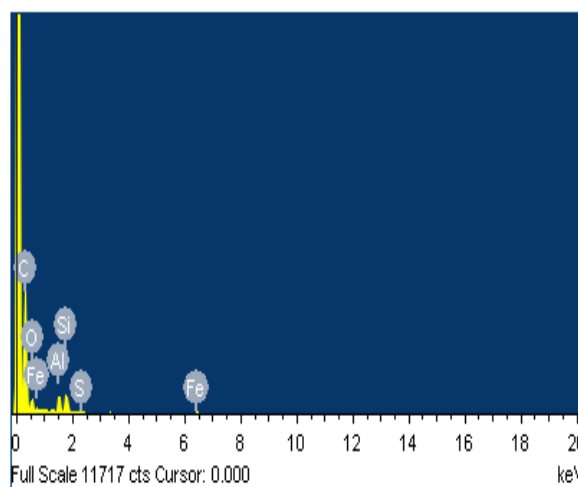


Fig. 4: EDX spectrum of graphite concentrate.

Table-14: Energy dispersive X-ray (EDX) analysis of graphite concentrate.

Element	Weight %	Atomic %
C	75.24	84.25
O	13.24	11.13
Al	3.14	1.57
Si	4.09	1.96
S	0.35	0.15
Fe	3.94	0.95
Totals	100.00	

Table-15: Particle size analysis of final graphite concentrate.

Sieve Number	Diam μm	Cumu %	Sieve Number	Diam μm	Cumu %	Sieve Number	Diam μm	Cumu %	Sieve Number	Diam μm	Cumu %
20	850	100	70	212	100	270	53	55.44	1000	13	7.28
25	710	100	80	180	99.82	325	45	46.56	1250	10	4.41
30	600	100	100	150	98.75	400	38	38.35	1670	8.5	3.18
35	500	100	120	125	96.31	450	32	30.92	2000	6.5	1.79
40	425	100	140	106	91.90	500	28	25.83	5000	2.5	0.01
45	355	100	170	90	85.46	600	23	19.38	8000	1.5	0
50	300	100	200	75	75.80	700	20	15.53	10000	1.3	0
60	250	100	230	63	65.55	800	18	13.03	12000	1	0

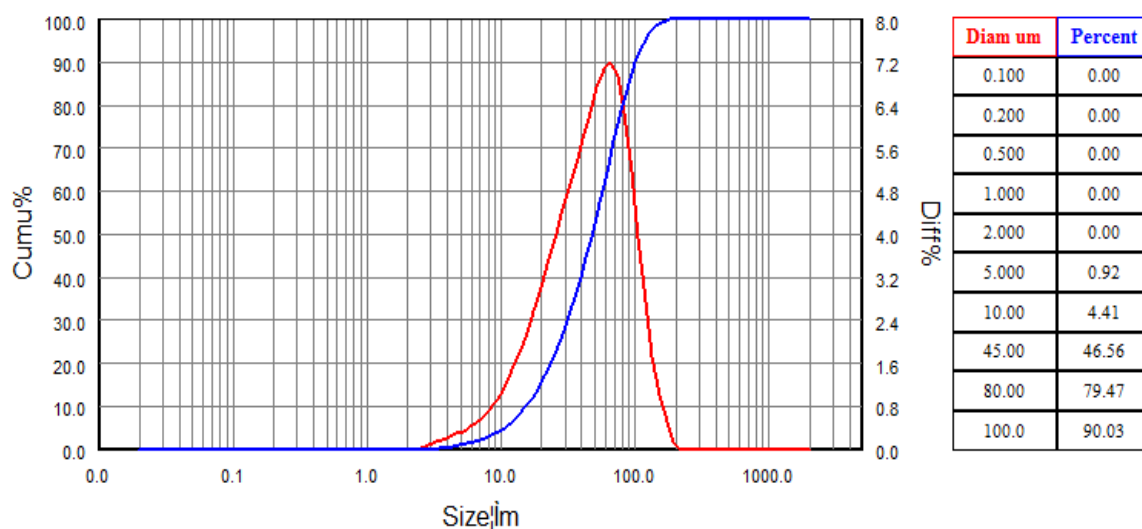


Fig. 5: Particle size analysis of final graphite concentrate.

Particle size analysis

The particle size analysis (Table-15; Fig. 5) shows that grain size of final graphite concentrate varies from 80 Mesh (180 μm) to 5000 Mesh (2.5 μm). However, the 98.75 % graphite material is finer than 100 Mesh (150 μm) and 100 % is finer than 70 Mesh (212 μm). The particle size finer than 200 mesh (75 μm) is 75.80%. The final concentrate may further be purified by chemical treatment for other industrial applications which require fine grain size and higher purity.

Conclusions

Beneficiation study of Azad Kashmir graphite ore through froth flotation technique revealed that foundry grade graphite concentrate can be produced by subjecting the rougher concentrate to two stage cleaning operation. It is also important to note that regrinding of the rougher concentrate up to 100% passing through 100 mesh before the two cleaning operations is essential for attaining a grade of more than 85.8% with an overall 86% recovery. Furthermore, re-circulation of cleaner and re-cleaner tailings to the flotation feed leads to a slight increase in grade and recovery of the product. However, for commercial exploitation of this deposit, the results

obtained from the bench scale beneficiation studies may also be confirmed by detailed beneficiation studies on pilot plant scale. SEM-EDX confirmed the multilayered flaky structure and carbon as the major constituent of the final graphite concentrate produced.

Acknowledgements

The authors are highly grateful to Dr. Shahid Ramey, Department of Solid State Physics, University of the Punjab, Lahore for his whole hearted support in X-ray diffraction study. The authors gratefully acknowledge the assistance offered by Mr. Mohabbat Khan and Mr. Ghulam Yasin during course of this work.

References

1. V. Ravichandran, C. Eswaraiyah and P. Manisankar, Beneficiation of low grade graphite ore deposits in Tamilnadu (India), *Ultra Chemistry*, **8**, 159 (2012).
2. K. R. Kazmi, M. A. Bhatti, M. S. Anwar and A. Mehmood, Beneficiation of Malakand Graphite Ore, *Pak. J. Sci. Ind. Res.*, **51**, 340 (2008).

3. K. R. Kazmi, M. S. Anwar, M. A. Bhatti and A. Mehmood, Kish beneficiation by floatation, *J. Chem. Soc. Pak.*, **30**, 11 (2008).
4. N. Vasumathi, T. V. V. Kumar, S. Ratchambigai, S. S. Rao, S. Prabhakar, G. B. Raju, B. R. Nayak, S. S. Kumar and U. Raman, Single reagent for graphite flotation, *Proceeding of The XIII International Seminar on Mineral Processing Technology*, Bhubaneshwar, India, p. 145 (2013).
5. H. Gautneb and E. Tveten, The geology, exploration and characterization of graphite deposits in the Jennestad area, Vesteralen, northern Norway, *NGU-Bull.*, **436**, 67 (2000).
6. D. W. Olson, *U.S. Geological Survey, Minerals Yearbook*, USGS press, USA, p. 32.1 (2012).
7. *U.S. Geological Survey, Mineral Commodity Summaries*, USGS press, USA, p. 69 (2014).
8. I. H. Khan, Development of Mineral-Based Industries, *Quarterly Science Vision*, **8**, 88 (2003).
9. Pakistan Minerals Working Group, *Bringing Mining in Pakistan up to International Standards*, Printo Graphic, Islamabad, Appendix 3 (2013).
10. V. K. Didolkar, V. A. Kumar, S. U. Pathak and R. H. Tupkaray, Beneficiation of low grade graphite ore from Multai area, Betul district, M.P., *Proceedings of Processing of Fines*, Jamshedpur, India, p. 177 (1997).
11. C. Chelgani, M. Rudolph, R. Kratzsch, D. Sandmann and J. Gutzmer, A Review of Graphite Beneficiation Techniques, *Min. Proc. Ext. Met. Rev.*, **37**, 58 (2016).
12. X. Niu, X. Li, J. Zhao, Y. Ren and Y. Yang, Preparation and coagulation efficiency of polyaluminium ferric silicate chloride composite coagulant from wastewater of high-purity graphite production, *J. Environ. Sci.*, **23**, 1122 (2011).
13. R. B. Rao and N. Patnaik, Preparation of high pure graphite by alkali digestion method, *Scand. J. Metall.*, **33**, 257 (2004).
14. F. H. Abd el-Rahiem, Application of column flotation for Egyptian graphite, *Tenside Surfact. Det.*, **41**, 104 (2004).
15. I. M. Joni, C. Panatarani, D. Hidayat, Setianto, B. M. Wibawa, A. Rianto and H. Thamrin, Synthesis and dispersion of nanoparticles, and Indonesian graphite processing, *AIP Conference Proceedings*, **1554**, 20 (2013).
16. O. Kaya and M. Canbazoglu, A study on the floatability of graphite ore from Yozgat Akdağmadeni (Turkey), *The Journal of Ore Dressing*, **9**, 40 (2007).
17. M. R. Patil, B. P. Ravi, M. V. Rudramuniyappa and P. S. Kumar, Characterization studies on graphite from Shivaganga area, Madurai, Dist., Tamilnadu, *International Journal of Innovative Science, Engineering and Technology*, **1**, 460 (2014).
18. X. Weng, H. Li, S. Song and Y. Liu, Reducing the entrainment of gangue fines in low grade microcrystalline graphite ore flotation using multi-stage grinding-flotation process, *Minerals*, **7**, 1 (2017).
19. F. Arduiniab, F. D. Giorgioab, A. Aminec, F. Cataldod, D. Mosconeab and G. Palleschiab, Electroanalytical characterization of carbon black nanomaterial paste electrode: Development of highly sensitive tyrosinase biosensor for catechol detection, *Analytical Letters*, **43**, 1688 (2010).