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BENEFICIATION OF LOW GRADE GRAPHITE ORE OF EASTERN INDIA BY TWO-STAGE GRINDING AND FLOTATION

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Abstract

A low grade graphite run-of-mine (r.o.m) ore from eastern India was studied for its amenability to beneficiation by flotation technique. The petrography studies indicate that the ore primarily consists of quartz and graphite with minor quantity of mica. It analyzed 89.89% ash and 8.59% fixed carbon. The ore was crushed in stages followed by primary coarse wet grinding to 212 µm (d80). Rougher flotation was carried out in Denver flotation cell to eliminate gangue as much as possible in the form of primary tailings with minimal loss of carbon. Diesel & pine oil were used as collector and frother respectively. Regrinding of rougher concentrate to150 µm (d80) was resorted to further liberate the graphite values and was followed by multi-stage cleaning. This two-stage grinding approach involving a primary coarse grinding and regrinding of rougher float followed by its multi-stage cleaning was found to yield required grade of concentrate for applications such as refractories, batteries and high temperature lubricants. This approach is supposed to retain the flake size of coarse, free and liberated graphite, if available, during primary coarse grinding and rougher flotation stage with minimal grinding energy costs as against the usual practice of single stage grinding in the case of many ores. A final concentrate of 8.97% weight recovery with 5.80% ash and 92.13% fixed carbon could be achieved.

Key words: *low grade graphite, liberation, froth flotation, regrinding, refractory*.

1. Introduction

Graphite is one of the two naturally occurring allotropes of crystalline carbon and the other being diamond. Graphite is lustrous black carbon mineral relatively soft, greasy with a hardness of 0.5 - 1.0 on Moh's scale [1]. The global graphite market consists of two main products namely microcrystalline graphite, called amorphous, and flake graphite [2]. Graphite generally occurs as a result of metamorphism of organic matter in sediments. Flake graphite is assumed to be derived from the fine-grained sediments rich in organic matter. As metamorphic grade increases, carbonaceous material converts to micro-crystalline graphite [1, 3]. Based on the size of the crystal flakes, flake graphite is classified and graded according to their graphitic carbon content and particle size.

Graphite beneficiation process depends upon the nature and association of gangue minerals present and can be enriched easily by flotation because of its natural hydrophobicity [3-5]. Froth flotation process is used widely as it helps in producing a high-grade graphite concentrate [6, 7] which finds applications in refractories, batteries and high temperature

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lubricants. Flotation utilizes the differences in the surface properties mainly the hydrophobicity of graphite [8-12] which is one among the factors in determining the separation efficiency by flotation. A low grade run-of-mine ore containing about 10% fixed carbon (FC) has to be invariably beneficiated before marketing.

In froth flotation, graphite ores are often subjected to a suitable hydrocarbon oil treatment to alter their hydrophobicity, enhance recovery, and /or improve selectivity [13]. Conventionally, the collector used in most of the flotation circuit is diesel oil in combination with pine oil as frother. The dosage of collector and frother has significant effect on flotation performance [14]. The common method of beneficiation is size reduction to enhance liberation followed by flotation [15]. The flotation is being carried out in different stages ranging from two to several stages depending upon the liberation characteristics of the ore to be treated. The present investigation aims at enrichment of a low grade Indian graphite ore by flotation technique with a two-stage grinding approach unlike the usual practice of single stage grinding in the case of many ores.

2. Experimental

2.1. Materials and methods

A low grade run-of-mine graphite ore was received from Jharkhand state of India. The ore was crushed in stages followed by mixing thoroughly. A representative sample was drawn for size and chemical analysis. The analysis of this sample and the results are shown in Table 1. The analysis of the graphite sample was determined as per Indian Standard, IS 14852:2000. For ash analysis, about 1 to 2 g of moisture free graphite sample was taken in a silica dish and kept in a muffle furnace and heated to 500°C within one hour and 775°C in two hours. A slow stream of air was maintained through the muffle furnace. When the carbon was completely removed as indicated by the absence of black particle upon stirring with a platinum wire, the temperature was further increased to 950°C and kept for one hour. The sample was then cooled in a desiccator and weighed. The ash calculation was carried out by dividing the weight of ash (g) by initial weight of sample taken (g).

Table 1. Analysis of graphite ore

Sample	Ash, %	Moisture, %	Volatile Matter, %	Fixed Carbon, %
Graphite (r.o.m)	89.89	0.12	1.40	8.59

2.2. Size analysis

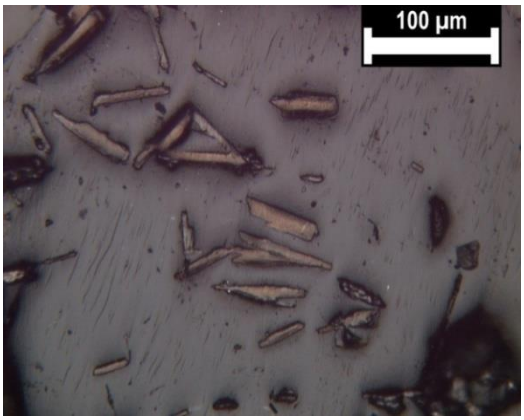
The particle size distribution of the stage-crushed graphite was carried out and the weight percentage retained on each screen along with their ash values are tabulated in Table 2. The calculated d_{80} of this graphite sample was found to be 605 μm. It is evident from the table that ash is evenly distributed across all size ranges with ash being above 88.83% in all size fractions. This implies that there are hardly any free and liberated graphite flakes in any size range and demands size reduction before attempting to recover the graphite values.

2.3. Mineralogy

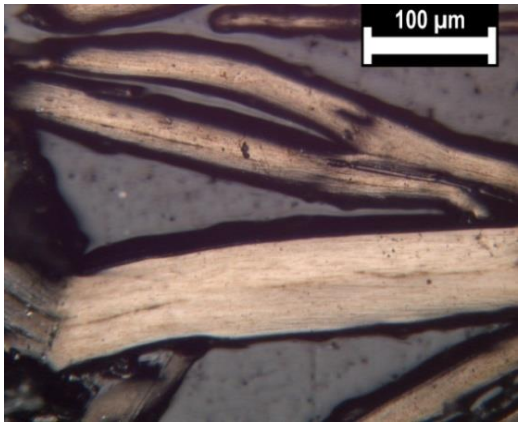
The mineralogical characterization of r.o.m graphite was carried out to determine the graphitic carbon content and graphite flake size. Petrographic images as in Fig. 1 under optical microscope indicated that the sample consists primarily of quartz and graphite in the form of both fine & thick flakes dispersed in the silica matrix, with minor quantity of mica (biotite).

Table 2. Sieve and ash analysis of stage-crushed graphite

S.No.	Size, µm	Wt., %	Ash, %	Ash Distribution, %
1	+850	12.13	91.01	12.23
2	-850+500	14.91	91.69	15.14
3	-500+300	17.49	90.02	17.45
4	-300+212	15.31	89.24	15.14
5	-212+106	22.86	90.92	23.02
6	-106	17.30	88.83	17.02



(a) Fine flakes of graphite dispersed within silica matrix



(b) Long flakes of graphite dispersed within silica matrix

Figure 1. Petrographic image of graphite

2.4. X-ray diffraction studies

The r.o.m graphite was subjected to x-ray diffraction studies for mineralogical phase analysis especially the identification of non-graphite minerals [16]. The characteristic x-ray of copper-Kα radiation with 0.154 nm wavelength was used in this diffraction study.

Form the x-ray diffractogram, predominant phase of quartz, minor fractions of graphite and traces of mica were observed.

2.5. Flotation tests

The flotation tests were conducted in Denver D-12 laboratory flotation machine, with a cell volume of about 3000 cm^3 and using conventional reagents, namely, diesel as collector and pine oil as frother for graphite flotation and sodium silicate as depressant for silica / silicate bearing minerals.

All the tests were conducted at 15% solids by weight at natural pH and impeller speed of 1200 rpm. The graphite ore slurry was conditioned with diesel and pine oil for 3 minutes each and the froth (float) was collected till froth formation ceased. The collected float and tailings were dewatered, dried, weighed and subjected to ash analysis.

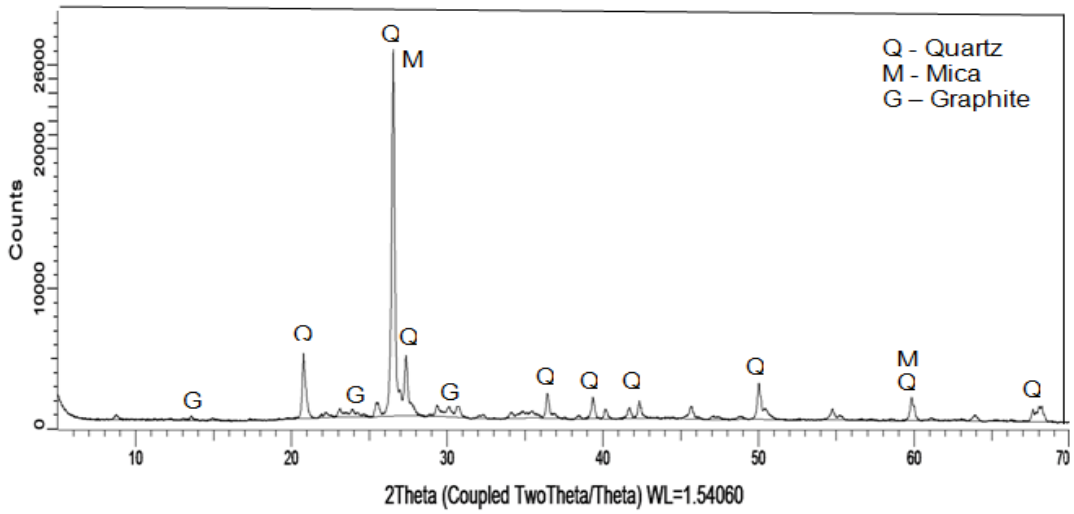


Figure 2. X-ray diffractogram of r.o.m graphite

3. Results and discussion

3.1. Grinding optimization followed by flotation

The stage-crushed graphite was subjected to primary grinding in a laboratory ball mill for different periods of grinding time (5, 7, 9, 11, 13 & 15 minutes) at 66% solids by weight. Sodium silicate (1.5 kg/t of feed) was added during grinding. The particle size analysis of the ground product at various time intervals of grinding is shown in Fig. 3.

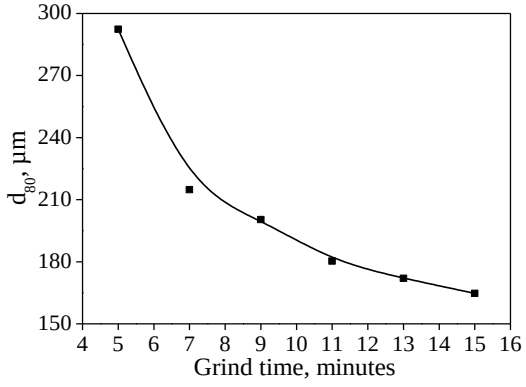


Figure 3. Size analysis at various grinding intervals

The size of the ground material was reduced to 292 µm from 605 µm during the initial five minutes grinding. It could be further reduced to 200 µm in another four minutes of grinding. The reduction in product size, henceforth, was gradual and reached 164 µm at the end of total fifteen minutes of grinding.

3.1.1. Effect of primary grinding time on flotation

The grinding time was increased from nil to 5, 7, 9, 11, 13 & 15 minutes and the ground products were subjected to rougher flotation. During rougher flotation, 0.0278 kg/t diesel and 0.0372 kg/t pine oil were added as reagents and this same dosage was maintained for all the tests on grinding variation studies. The float and tailings obtained were dried and subjected to ash analysis.

The test results are tabulated as shown in Table 3 and it could be seen that the graphite grade and recovery varied within a narrow range. Beyond 5 minutes grinding time, there is no or marginal improvement in grade and recovery. Though the yield is almost constant

from 5 minutes grinding time (d_{80}: 292 μm) onwards, the ash distribution in the tailings at various grinding times remained constant around 91%. Further grinding would result in expending grinding energy with no significant gain in grade and recovery. At this coarse primary grinding, 86.49% of the feed could be rejected as the tailings (assaying 96.35% ash). Hence the grinding was optimized at 292 μm.

Table 3. Effect of grinding time on graphite grade and recovery

Grinding time, minutes (d_{80}, μm)	Products	Wt., %	Ash, %	Ash Dist., %
0 (605)	Float	14.69	70.23	11.18
	Tailings	85.31	96.16	88.82
5 (292)	Float	13.51	63.57	9.34
	Tailings	86.49	96.35	90.66
7 (214)	Float	13.56	63.87	9.41
	Tailings	86.44	96.48	90.59
9 (200)	Float	13.59	62.30	9.12
	Tailings	86.41	97.61	90.88
11 (180)	Float	13.35	59.66	8.60
	Tailings	86.65	97.68	91.40
13 (172)	Float	12.97	62.45	8.71
	Tailings	87.03	97.52	91.29
15(164)	Float	13.25	62.99	8.96
	Tailings	86.75	97.70	91.04

3.1.2. Effect of variation in depressant (sodium silicate) dosage

Sodium silicate dosage was gradually increased from 0.5 to 2.5 kg/t during grinding and flotation was carried out at fixed diesel & pine oil dosages i.e., 0.0278 kg/t & 0.0372 kg/t respectively. The results of the same are shown in Table 4.

It appears variation of sodium silicate has little or marginal effect on the separation. The weight recovery and ash of floats hover around 20% and 46% respectively. A minimal dosage of sodium silicate (0.5 kg/t) would suffice the rejection of gangue consisting of silica and silicates into tailings. At this, 81.86% of the feed with 97.49% ash could be rejected as the tailings

Table 4. Effect of variation in sodium silicate on flotation

Sodium silicate, kg/t	Products	Wt., %	Ash, %	Ash Dist.,%
0.5	Float	18.14	45.91	9.45
	Tailings	81.86	97.49	90.55
1.0	Float	20.16	45.81	10.56
	Tailings	79.84	97.94	89.44
2.0	Float	20.36	45.95	10.74
	Tailings	79.64	97.65	89.26
2.5	Float	19.83	46.63	10.58
	Tailings	80.17	97.41	89.42

3.1.3. Effect of variation in collector (diesel) dosage

The sodium silicate dosage was maintained at 0.5 kg/t during grinding. The effect of variation in diesel dosage on flotation was

studied keeping pine oil dosage constant at 0.0372 kg/t. The results of the same are given in Table 5.

Table 5. Effect of variation in diesel on flotation

Diesel, kg/t	Products	Wt., %	Ash, %	Ash Distribution, %
0.0278	Float	18.14	45.91	9.45
	Tailings	81.86	97.49	90.55
0.0556	Float	17.03	49.26	9.33
	Tailings	82.87	98.35	90.67
0.0834	Float	18.86	48.63	10.38
	Tailings	81.14	97.62	89.62
0.1112	Float	18.27	52.00	10.63
	Tailings	81.73	97.72	89.37
0.1390	Float	18.62	47.27	9.98
	Tailings	81.38	97.58	90.02

As the dosage of diesel is increased from 0.0278 to 0.1390 kg/t, the weight recovery of float varied from 17.03% to 18.62%, whereas its ash content changed from 45.91% to 52.00%. The higher values of ash in the floats at the higher dosages of diesel could be attributed to reporting of interlocked particles of graphite – silica, still remaining in the pulp, into the float, thus diluting its grade. Thus, the dosage of diesel was optimized at 0.0556 kg/t as the ash rejection into the tailings was maximum at 90.67%. At this dosage, yield of the float is 17.03% with 49.26% ash in it.

3.1.4. Effect of variation in frother (pine oil) dosage

A series of flotation tests was carried out at 0.5 kg/t sodium silicate during grinding and constant dosage of diesel oil at 0.0556 kg/t during flotation tests.

Pine oil was varied from 0.0372 to 0.1860 kg/t dosages. The results of the same are shown in Table 6.

Table 6. Effect of variation in pine oil on flotation

Pine Oil, kg/t	Products	Wt., %	Ash, %	Ash Distribution, %
0.0372	Float	17.03	49.26	9.33
	Tailings	82.87	98.35	90.67
0.0744	Float	18.99	44.55	9.70
	Tailings	81.01	97.27	90.30
0.1116	Float	19.11	45.68	9.96
	Tailings	80.89	97.56	90.04
0.1488	Float	20.36	51.72	11.94
	Tailings	79.64	97.56	88.06
0.1860	Float	20.24	51.56	11.81
	Tailings	79.76	97.71	88.19

The ash distribution is minimum at 9.33% in the float and ash rejection into tailings is maximum at 90.67% at pine oil dosage of 0.0372 kg/t. As the pine oil dosage is increased further to 0.1860 kg/t in subsequent tests, more of ash reported to the floats, thus diluting the grade of the floats. This could be due to physical entrainment of fine gangue in the water that flows along with the froth / float at higher dosages of frother. Hence, the dosage of pine oil was optimized at 0.0372 kg/t during rougher flotation.

Thus the optimum conditions for rougher flotation are 0.0556 kg/t diesel and 0.0372 kg/t pine oil. At these optimized conditions, rougher concentrate of 17.03% weight recovery at 49.26% ash content was obtained. The primary tailings, at this stage analyzed 98.35% ash with minimal loss of 0.20 % fixed carbon in it.

4. Regrinding and cleaning of rougher concentrate

After rejecting the gangue to the maximum extent possible at the rougher flotation stage that was preceded by primary coarse grinding, it is thought prudent to subject rougher float to regrinding in order to further liberate interlocked values. In this connection, optimization of regrinding size was carried out using nominal dosage of sodium silicate (0.25 kg/t) during regrinding. This was followed by multi-stage cleaning to reduce the ash value in the final concentrate to the maximum extent possible with respectable weight recovery.

4.1. Effect of variation in regrinding time of rougher concentrate

Regrinding of rougher float obtained at different grinding times was subjected to 8-stages of cleaner flotation using 0.0556 kg/t diesel and 0.0372 kg/t pine oil at the first stage of cleaning. No further addition of reagent was resorted to in the remaining stages of cleaning. The results of the tests are shown in Table 7.

Table 7. Cleaner flotation tests on the regrinding of rougher concentrate

Regrinding time, min. (d_{80}, μm)	Products	Wt., %	Ash, %	Ash Distribution, %
15 (185)	Final Conc.	9.33	12.39	1.29
	Cl. Tails	8.30	93.83	8.6
	Primary Tails	82.37	98.27	90.05
20 (165)	Final Conc.	8.97	5.80	0.58
	Cl. Tails	8.06	97.63	8.75
	Primary Tails	82.97	98.35	90.67
30 (155)	Final Conc.	9.13	7.44	0.76
	Cl. Tails	8.20	95.98	8.75
	Primary Tails	82.67	98.23	90.49
40 (144)	Final Conc.	9.20	6.58	0.67
	Cl. Tails	8.53	94.26	8.95
	Primary Tails	82.27	98.75	90.38

From the results, it is clear that it is possible to obtain a graphite concentrate with less than 10% ash content.

It is necessary for grinding the rougher concentrate up to 165 μm (d_{80}) followed by multi-stage cleaning in conventional flotation cells. The best concentrate obtained has 5.80% ash in it with weight recovery of 8.97% (with respect to primary feed). A conceptual flow-sheet was developed based on the findings of the investigation and shown as Fig. 4. The fixed carbon analysis was carried out on the final concentrate sample and the results are as shown in Table 8.

Table 8. Analysis of final graphite concentrate

Sample	Ash, %	Moisture, %	Volatile Matter, %	Fixed Carbon, %
Final concentrate	5.80	0.35	1.67	92.13

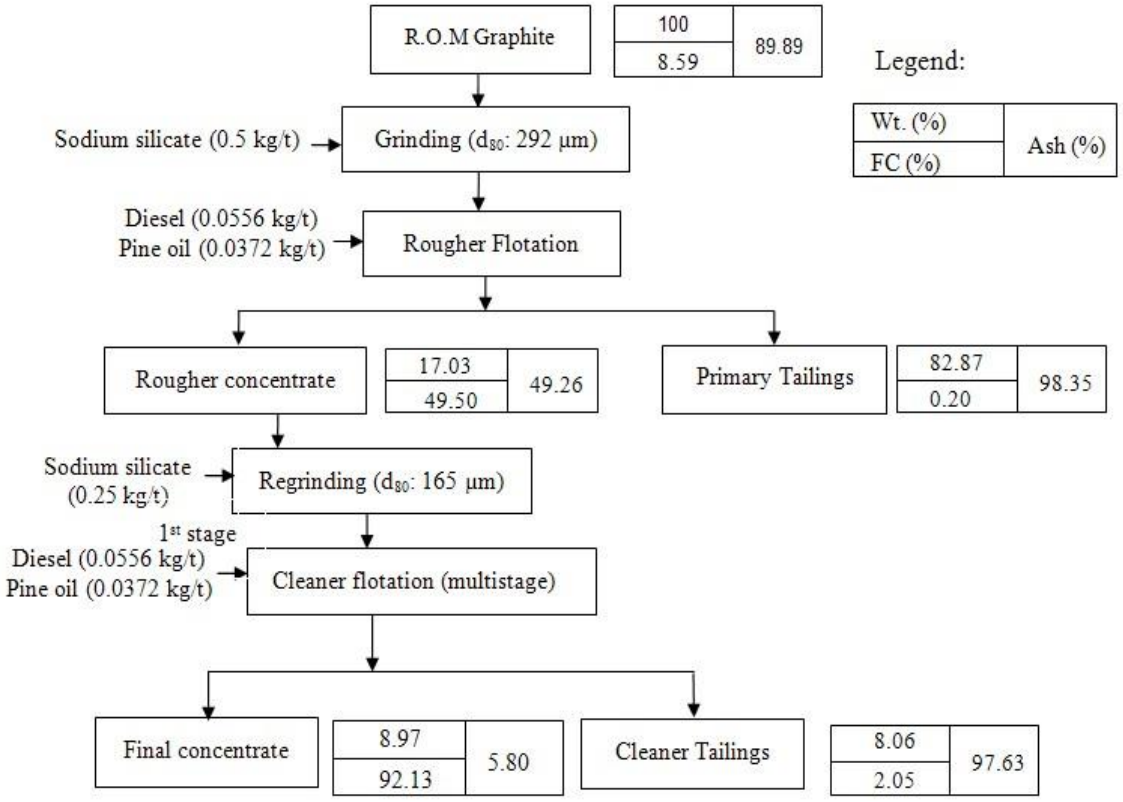


Figure 4. Conceptual flow sheet for beneficiation of low grade graphite ore by flotation

5. Conclusions

A primary coarse grinding of low grade graphite ore to 180 µm (d_{80}) with 0.5 kg/t sodium silicate as depressant for silica bearing gangue followed by rougher flotation at natural pH, 0.0556 kg/t diesel and 0.0372 kg/t pine oil yields 17.03% rougher concentrate with 49.26% ash. 82.87% of the feed with 98.23% ash and minimal loss of 0.2% fixed carbon could be rejected as primary tailings. Regrinding of rougher concentrate followed by multi-stage cleaning enhanced the graphite grade to 92.13% fixed carbon and 5.80% ash with 8.97% weight recovery. This approach of two-stage grinding followed by multi-stage cleaning proves to be an efficient beneficiation technique especially for very low grade graphite ore. From this, a conceptual flow sheet was developed for this ore which could be viable and cost effective. The concentrate so generated finds applications in refractories, batteries and as high temperature lubricant.

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