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Characterization and selection of flotation reagents to improve the graphite ore beneficiation

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Abstract

A detailed characterization study was conducted on Sivaganga graphite ore deposit. The representative graphite samples of rod mill discharge were collected from the beneficiation plant of Tamilnadu Minerals Limited (TAMIN). The rod mill discharge was subjected to flotation to enrich the carbon values. The rod mill discharge and products obtained from flotation were carefully characterarized by XRD, Zeta probe. Flotation reagent functional groups identification was carried out by Fourier Transform Infrared Spectroscopy (FTIR). The x-ray diffraction results of rod mill discharge was revealed that in the feed material, graphite, kaolinite and quartz mineral phases are present whereas in its ash sample quartz and hematite mineral phases are present. It was observed that graphite, kaolinite and quartz are present in concentrate and tailings samples like feed sample. However, only quartz phase has been observed in tailings ash sample. The zeta potential study clearly show that the combination of MIBC, ethyl alcohol and kerosene (i.e., MEK) having the point of zero charge at pH around 8. From this it is concluded that the MEK combination is work better for flotation than other reagents. Various frothers selected for FTIR study. From this study, it is concluded that MIBC yields better efficiency than other frothers.The possible reasons could be due to differences in their functional groups. Combination of MIBC and ethyl alcohol ratio of 90:10 frother provides better efficiency than the individual frother.

Key words: Floatation; characterization; graphite; FTIR

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1. Introduction

Tamilnadu Minerals Limited (TAMIN) has graphite beneficiation plant at Sivaganga. The plant was designed with rated capacity of 200 tons per day to process feed material with an average grade of 14 to 15% (F.C) fixed carbon to produce 28 tons per day of graphite concentrate having 96% F.C. The graphite ore sample is black-gray colored soft friable flakes associated with predominant amount of siliceous gangue. As the plant did not attain the rated designed capacity, the research work was carried out to optimize the plant capacity and also to find out the technical bottle neck of the process. The characteristics of the reagents and ore are one of the causes related to plant performance. Graphite has become indispensible for a variety of end users in modern industries due to its unique properties like high heat resistance, electrical conductivity, softness, refractoriness, chemical inertness and low coefficient of friction. It is used in different variety of industries as raw material. The high quality graphite demand is increasing day to day[1-2]. Therefore, to meet the demand of the downstream industries to produce high quality graphite, it requires a basic understanding of ore and reagents characteristics to produce desired concentrate in the beneficiation process. As graphite is hydrophobic material and its liberation is at finer size, flotation is the ultimate process to upgrade the graphite to achieve required quality by physical beneficiation. The associated mineral phases in graphite ore affect the flotation performance. Hence, both the grade and recovery of graphite concentrate in beneficiation process detoriate. The degree of hydrophobicity of various associated minerals can be controlled by direct surface chemical action of flotation reagents[3-6]. FTIR and electro-kinetic studies on the coal from same source were carried out to evaluate the oxidation characteristics using aliphatic alcohols as pre-treatment reagents[7-8]. Black oil was used to improve the floatability of the coal particles[9]. Characterization of the low grade calcareous graphite ore was studied and reported the ore consists of graphite, calcite and quartz as major minerals[10].

In this work, an attempt has been made to characterize the rod mill discharge, floatation concentrate and tailings of the process. In view of the above, a detailed characterization study is conducted on rod mill discharge, float concentrate, tailings and reagents to understand the influence and effect on beneficiation process.

2. Materials and Methods

2.1. Materials

The graphite with varying amounts of fixed carbon content and associated minerals with diverse ore types are noticed in Sivaganga deposit. The rod mill discharge samples were collected in different time intervals for the period of 15 days to get more accurate representative samples. Representative graphite sample from the plant was taken and subjected to flotation. Commercial grade forthers such as pine oil, MIBC, Nalco-9840, eucalyptus oil, ethyl alcohol and collectors such as kerosene and diesel oil were taken into consideration for characterization studies.

2.2. Methods

2.2.1. *Physical and Chemical Characteristics:*

The size analysis is carried out using

standard BSS sieves of rod mill discharge. Proximate analysis was carried out on rod mill discharge at different size fractions. The rod mill discharge, final concentrate and rougher tailings were subjected to X-ray diffraction analysis for the phase identification. Zeta potential measurements were carried out by Zeta probe instrument to know the point of zero charge of material as well as with reagents. Fourier Transform Infrared Spectroscopy (FTIR) was done to identify the functional groups present in the reagents.

3. Experimental

3.1. *XRD Studies :*

The phase characterization of samples were done by using X-ray powder diffract meter (Model: X'pert Pro, Netherland) equipped with Cu target (CuK =1.54056 A°) operating at 40 kV and 30 mA. The diffractograms were recorded from 6 to 70° 2θ with a scan speed of 3 sec/step and a step size of 0.017° 2θ. The diffraction lines were identified for different phases present in the samples using high score software.

3.2. *Zeta potential Studies :*

All particles in suspension exhibit a surface charge. Knowledge of zeta potential is critical for the optimization of sample processing and is a simple method for quality control. Zeta potential can also be used to predict the stability of formulation. Additionally, a quantification of zeta potential is useful for the prediction of interactions in a multi-component system. Zeta potential measurements were carried out by Zeta probe instrument from colloidal dynamics, UK to know the point of zero charge of material as well as with reagents.

3.3. *FTIR Studies :*

Fourier Transform Infrared Spectroscopy is a widely used technique to identify the functional groups present in the organic and inorganic reagents. Diffused reflectance Fourier transform infrared spectra (DRIFTS) of samples were recorded on FTIR system (spectrum GX model, Perkin Elmer instrument) having DRIFTS attachment supplied by Harrick, USA. The spectra were recorded from 500 to 4000cm^{-1} and KBr was used as reference.

4. Results and Discussion

4.1. *Physical and chemical characteristics of rod mill discharge :*

The size and proximate analysis of rod mill discharge of different size fractions were determined to know the liberation characteristics. The results are given in Table 1. From the table, it has been observed that the fixed carbon of average feed material is 14.83 % (F.C) and 5.68 % volatile matter (V.M). The representative sample of rod mill product true density was measured by using pycnometer. The true density and bulk density of product found to be 2.6 and 1.6 gm/cc respectively.

4.2. *Mineralogical characteristics :*

The representative sample of graphite ore was used to study the mineralogical characteristics using optical microscope. The quantitative mineralogical analysis results of graphite sample are given in Table 2. It indicates that the raw material predominantly consists

Table 1. Size and proximate analysis of rod mill discharge

Mesh (BSS)	wt., %	F. C., %	V. M., %	ash, %
-28+36	13.34	17.36	5.20	77.44
-36+44	11.70	18.83	5.15	76.02
-44+52	6.63	18.23	4.80	76.97
-52+60	5.60	17.98	5.12	76.90
-60+72	16.77	16.04	5.19	78.77
-72+100	12.63	12.66	5.23	82.11
-100+150	9.57	11.22	5.36	83.42
-150+200	6.33	10.37	6.13	83.50
-200	17.43	10.82	8.91	80.27
Head(calculated)	100	14.83	5.68	79.49

of quartz mineral with subordinate amounts of graphite; clay, goethite/limonite, carbonates, feldspar, hematite and pyrite are also noticed in trace level.

Table 2. Mineralogy characteristics of the graphite sample

Minerals phases	percent
Graphite	15.0
Quartz	60.0
Clay	13.0
Goethite / Limonite	7.0
Carbonates (Ca & Mg)	1.5
Feldspar	3.0
Hematite	Traces
Pyrite	Traces

4.3. *Flotation studies :*

The flotation studies were carried out in mechanical laboratory sub-aeration flotation cell. The volume of cell taken for this study was 10 lit. The rod mill discharge sample of 2 kg was subjected to flotation experiments. The sodium silicate was used as dispersing reagent to depress the silicate phase minerals. The sodium carbonate was used as pH regulator. The pH of slurry was maintained at around 8.5. The commercial grade diesel oil was used as collector whereas commercial grade MIBC used as frother and ratio of MIBC and diesel oil was 1:9. As per plant practice, all reagent dosages were maintained. The amount of sodium silicate used in this study was 200 gm/ton of feed material. Similarly, diesel oil was used 100 ml per ton of feed material and whereas MIBC was 10% of the collector dosage. The experiments were carried out at 1500 rpm of rotor speed. The conditioning time of reagents in the slurry was allowed for 3 minutes. Then water (at 8.5 pH) was added to maintain 20% solid concentration in the slurry. The air was released to generate the air bubbles. The concentrate and tailings were collected separately. The concentrate was again ground and cleaned

Table 3. Proximate analysis of flotation concentrate and tailings

Details	wt., %	F.C, %	V.M, %	ash, %
Flotation conc.	14	95.27	1.35	3.38
Rougher tails	79	1.2	6.5	92.3
Cleaning tails 1	5	5.6	8	86.4
Cleaning tails 2	2	12.37	7.22	80.41
Head	100	14.81	5.86	79.33

further in same cell as per the plant circuit. The concentrate and tailings in first stage cleanings were collected separately. The concentrate of first stage cleaning was subjected to laboratory model column flotation at quality control laboratory, Sivaganga. The geometrical dimension of flotation column is 5.08 cm diameter and 180 cm height. The final cleaning stage was carried out in column flotation by following the standard procedure of operation. The concentrate and tailings were collected separately. All stages of tailings and final concentrate from column flotation were subjected to proximate analysis. Proximate analysis of flotation concentrate and tailings are given in Table 3.

4.4. *Phase characterization :*

The X-ray diffraction patterns of rod mill discharge, flotation concentrate and tailings and their respective ash are shown in Fig. 1-3. The XRD results of rod mill discharge and its ash are shown in Fig. 1. It has been observed that in the feed material, graphite, kaolinite and quartz mineral phases are present whereas in its ash sample quartz and hematite mineral phases are present. The diffraction peaks for kaolinite mineral composition has not been observed in ash sample because it decomposes during ash analysis at 950^{o}C. Alumina peak might have been seen in XRD pattern of ash due to kaolinite decomposition but it does not appear because of its amorphous nature. The hematite phase is appearing in ash of feed material due to oxidation of amorphous goethite mineral during ash analysis.

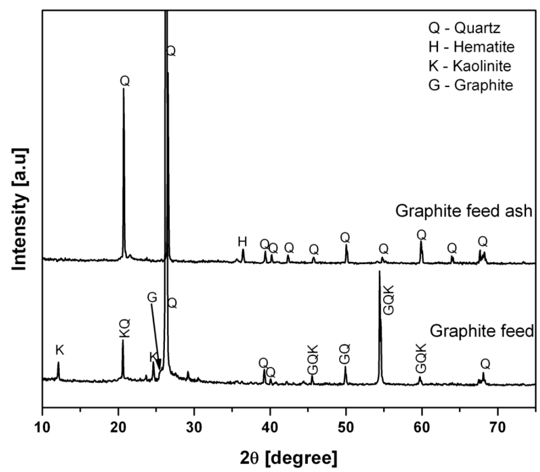

Fig. 1. X-ray powder diffraction patterns of graphite feed and its ash

XRD results of concentrate, tailings and their respective ash samples are shown in Fig. 2 and Fig. 3 respectively. It has been observed that graphite, kaolinite and quartz are present in concentrate and tailings samples like feed sample. It has been seen that the mineralogical composition of concentrate ash is same as feed ash sample. However, only quartz phase has been observed in tailings ash sample.

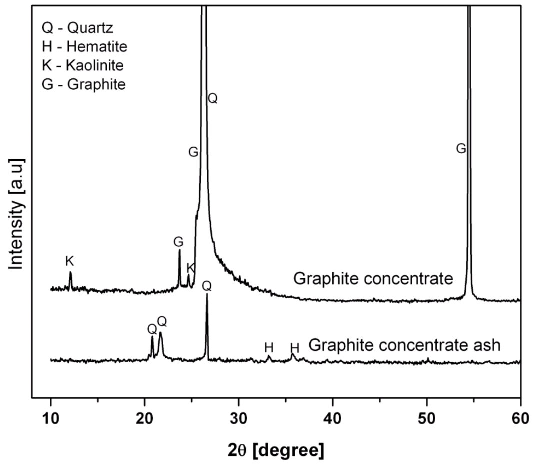

Fig. 2. X-ray powder diffraction patterns of graphite concentrate and its ash

It needs to mention that the iron phase minerals are floating along with graphite concentrate. Iron phase minerals may be available in the tailings which have not been detected by XRD due to their trace level.

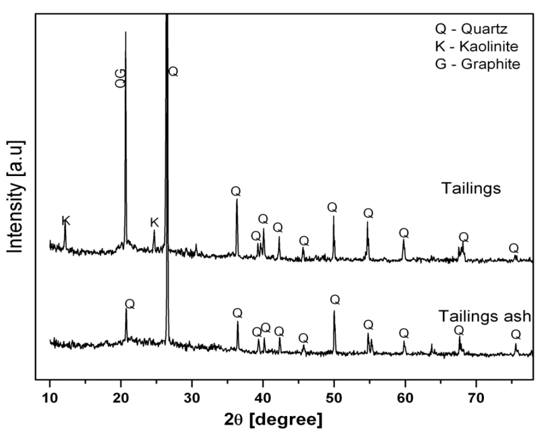

Fig. 3. X-ray powder diffraction patterns of tailings and its ash

4.5. *Zeta potential studies :*

Zeta potential is dependent on the nature of both the particle and the suspension formulation. Zeta potential can help you to understand and control colloidal suspensions. More recently for measurements with relatively concentrated suspensions, instruments based on the electroacoustophoretic effect are available[11-12]. In this work, the zeta potential measurement of graphite ore, flotation concentrate and tailings were measured by using zeta meter. The zeta potential versus pH is shown in Fig. 4 for graphite ore, flotation concentrate and tailings. From this figure, it is observed that the graphite ore and tailings show a negative charge. However, the final concentrate has the point of zero charge at around pH 5.3. The zeta potential measurements were also conducted on final concentrate by adding different collectors and also frothers at the dosage of 5 drops. The effect of frother at 5 drops of reagent dosage were measured and shown in Fig. 5. From the figure, it is observed that the curve of graphite with MIBC and diesel oil clearly shows the particles are positively charged. However, pure graphite concentrate has the point of zero charge at around pH 8.7. Since the graphite ore is negatively charged from the evidence of zeta potential results, the polar reagent is more preferable to achieve the better flotation concentrate. In Fig. 5, it is clearly show that the combination of MIBC and ethyl alcohol with kerosene (i.e., MEK) having the point of zero charge at pH around 8. It is concluded that the MEK combination is work better for flotation than other reagents as indicated from Fig. 5.

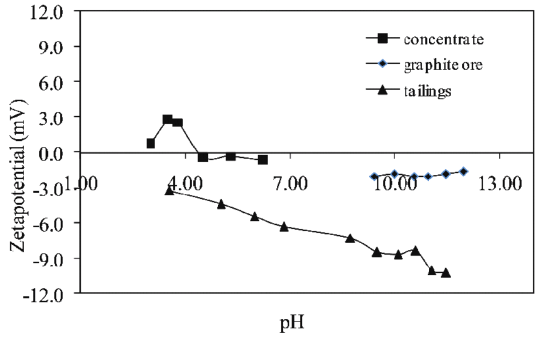

Fig. 4. Zeta potential results of graphite ore, concentrate and tailings

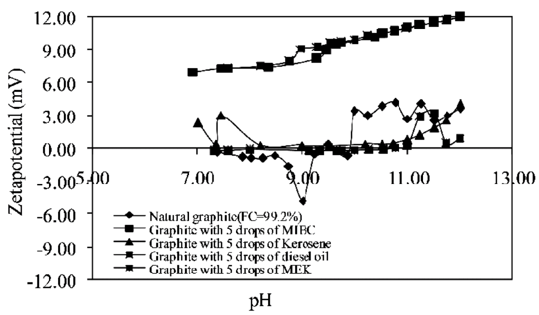

Fig. 5. Zeta potential results of pure graphite and with reagents

4.6. *FTIR Studies :*

FTIR experiments were carried out to identify the functional groups present in the organic and inorganic reagents. In flotation, various reagents interact with mineral surfaces based on their surface charge. FTIR spectra of various flotation reagents such as frothers, collectors, depressant and pH regulator were considered to know the functional groups and their response to the flotation.

Kerosene and diesel oil are used as a collectors for flotation of graphite ore. The collector changes the hydrophilic to hydrophobic nature of graphite which facilitates the flotation process. To understand the reagents efficiency, an individual FTIR spectrum of kerosene and diesel oil has been recorded and shown in Fig. 6 and Fig. 7 respectively. The spectral assignments from FTIR are given in Table 4 and 5. It was observed that the bands at 2963, 2924, 2859 cm^{-1} for alkane groups are more prominent in case of kerosene compared to the diesel oil. FTIR spectra of kerosene and diesel oil adsorbed graphite concentrate are recorded and their spectrum is shown in Fig. 8 and their spectral assignments are given in Table 6. The graphite without adsorbate is also shown for comparison purpose. However, the difference in the spectral band intensity has been noticed. The intensity of spectral bands of graphite sample decreased after adsorption of kerosene and diesel oil, but this decrease in intensity is more for kerosene adsorbed graphite sample compared to diesel oil adsorbed. This reveals that kerosene has more strongly adsorbing on graphite surface (compared to diesel oil) to yield a better performance.

Various frothers such as pine oil, MIBC, Nalco-9840, eucalyptus oil and ethyl alcohol have been used in the graphite flotation experiments to obtain the optimum efficiency. As these reagents are having different functional groups, in order to identify the various functional groups, FTIR spectrum of each reagent has been measured and compared. Among the frothers used in this study, mixed frother containing MIBC and ethyl alcohol 90:10 ratio has shown high performance in the flotation experiments. When these two reagents were used individually, their performances are found to be poor compared to the mixed MIBC and ethyl alcohol 90:10 frother ratio. However, while comparing the MIBC and ethyl alcohol, MIBC yields better efficiency. The possible reasons could be due to differences in their functional groups. Hence, it can be said that MIBC and ethyl alcohol (90:10) mixture frother provides better efficiency than the individual frother.

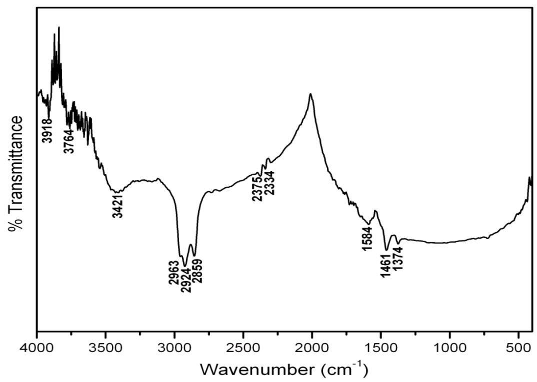

Fig. 6. FTIR spectrum of kerosene

Table 4. Kerosene FTIR spectral band position and their assignments

Band position	Spectral assignments
3764	O-H stretching group
3421	O-H stretching group, NH stretching group
2963	C-H stretching
2924	C-H stretching
2859	C-H stretching
2375	CO_2
2334	CO_2
1585	C-H stretching
1461	CH_2
1374	Nitro group

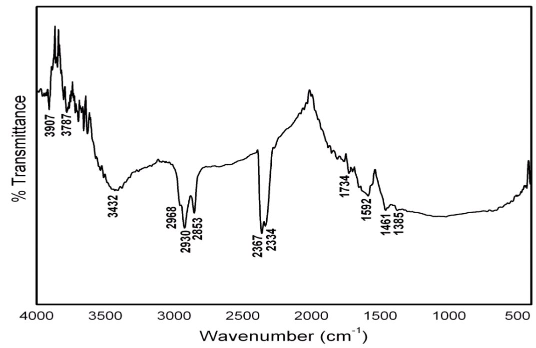

Fig. 7. FTIR spectrum of diesel oil

Table 5. Diesel oil FTIR spectral band position and their assignments

Band position	Spectral assignments
3787	O-H stretching group
3432	O-H stretching
2968	C-H stretching
2930	C-H stretching
2853	C-H stretching
2367	CO_2
2334	CO_2

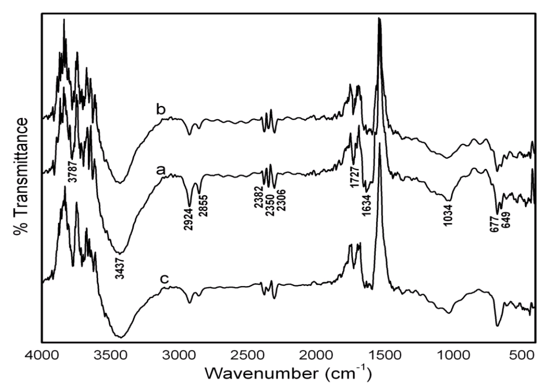

Fig. 8. FTIR spectrum of (a) graphite (b) graphite with kerosene (c) graphite with diesel oil

Table 6. FTIR spectral band position and their assignments (a) Graphite (b) Graphite with kerosene (c) Graphite with diesel oil

Band position	Spectral assignments
3787	O-H stretching of hydroxyl group
3473	O-H stretching of hydrogen banded hydroxyl group H_2O
2924	C-H stretching
2855	C-H stretching
2382	CO stretching CO_2
2350	CO stretching CO_2
2306	CO stretching CO_2
1727	aldehyde C=O stretching
1634	O-H bending H_2O

Conclusions

The flotation studies were carried out on Sivaganga graphite plant rod mill discharge containing average feed grade of 14.81%. From the flotation, the rod mill discharge was upgraded from 14.81to 95.27%. By x-ray diffraction analysis, different mineral phases present in rod mill discharge, flotation concentrate and tailings were identified. It was observed that graphite, kaolinite and quartz are present in concentrate and tailings same like feed sample. However, only quartz phase has been observed in tailings ash sample.

The Zeta potential study clearly show that the combination of MIBC and ethyl alcohol with kerosene (i.e., MEK) having the point of zero charge at pH around 8. It is concluded that the MEK combination is works better than other combinations. The functional groups were identified for different flotation reagents used in the present investigation. Among the collectors kerosene has more strongly adsorbing on graphite surface (compared to diesel oil) to yield a better performance. From this study, it is concluded that individual MIBC yields better efficiency compared to other frothers. However, combination of MIBC and ethyl alcohol (90:10 ratio) shows better flotation performance in terms of gas hold-up.

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