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THERMAL AND STRUCTURAL STUDY OF LOW GRADE GRAPHITE ORE FROM SHIVAGANGA, INDIA – ITS IMPLICATIONS IN BENEFICIATION PROCESS

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Abstract

In this paper an attempt has been made to characterize the low grade calcareous graphite ore from Shivaganga region, India. By judicious combination of structural, thermal and chemical analytical techniques, the liberation size of graphite as well as estimation of minerals are determined to establish a feasible beneficiation process. This data show a good correlation. The ore consists of graphite, calcite and quartz as major minerals. The *d*-values and decomposition of calcite are found maximum at two size fractions i.e., +500 and below 90 microns. The TG and chemical analysis data on quantitative minerals estimation confirms that calcite significantly liberates below 90 micron size fraction and accounts for 60% calcite and 10% graphite minerals distribution. The DTA data show that calcite decomposes between 700–850°C and graphite starts combustion at 850°C. In view of this, to achieve calcite free graphite the ore needs to be calcined below 850°C and ground to 80% passing 75 micron size prior to flotation.

Keywords: DTA-TG, graphite, structural study, XRD

Introduction

Shivaganga graphite ore has been characterized by a few researchers and academicians. Most of these studies are restricted to microscopic studies only. Based on these studies recommendations were also made to select the beneficiation process [1–4]. Thermal analysis of simple graphite ore and its implications in beneficiation process was studied by Navin Kumar *et al.* [5]. Published data are not available on the use of structural study for liberation size and selection of beneficiation route for graphite ore. However, all the methods viz. microscopic, thermal and structural studies have certain limitations. Estimation of liberation size of graphite by grain counting in the microscope could represent wrong results especially at size fractions below 100 microns as the most of the grains are smeared by graphite. It is also found difficult to identify the gangue minerals present in the graphite flakes [6]. In thermal study, if the ore contains both graphite and calcite, the total mass loss is reported by both the minerals. Similarly if the ore contains quartz and graphite, the diffraction

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intensities interfere with each other in the thermal study. Hence one method of analysis is usually not sufficient to characterize the ore and combination of different methods is required. So far no attempt has been made to characterize the ore for determining the liberation size to graphite as well as recommending the beneficiation route by using combined structural, thermal and chemical analytical techniques.

In this paper characterization and assessment of liberation size of graphite has been attempted by using combined structural, thermal and chemical analytical techniques to establish most economic and environment friendly beneficiation process.

Materials and methods

The graphite ore containing 15% FC and 59.7% acid solubles was procured from M/s Saak Trading Corporation, Madurai, Tamilnadu, India. The ore is a schistose of calc-silicate flaky graphite rock and friable to compact in nature. A representative sample was crushed stage wise to below 500 micron size and subdivided for present investigations. The samples were subjected to different calcination temperatures and acid leaching. Another portion of this sample was subjected to wet classification at different sizes. All the calcined, acid leached samples and each narrow size range fractions were subjected to XRD, DTA, proximate and chemical analysis.

The X-ray unit, Phillips automatic diffractometer, having autodivergent slit, graphite monochrometer and scintillation detector was used with CuK$_\alpha$ radiation at a scanning speed of 2^o (2θ) min^{-1}. The DTA/TG of the sample was carried out using Stanton Redcraft STA-781 and calcinated alumina as a reference material. The analysis was carried out at constant heating rate of 10^{o}C min^{-1} in a static air atmosphere and the sensitivity was kept constant during the complete DTA run. Calcination was carried out in a muffle furnace. Concentrated hydrochloric acid (AR Grade) was used for leaching of calcite mineral. The fixed carbon was determined at 850^{o}C for 3 h. The CaO content was determined by standard wet chemical methods.

Results and discussion

X-ray diffraction

X-ray diffraction pattern of different pretreated samples are shown in Fig. 1 (Figs 1a to 1e). It can be seen from Fig. 1a, that the graphite sample oven dried at 105^{o}C exhibit the presence of minerals such as graphite, calcite, quartz, kaolinite, etc. It is interesting to observe that when this sample is calcined at 500^{o}C, the kaolinite mineral phase starts disappearing in the sample (Fig. 1b). At 700^{o}C calcination, the kaolinite phase totally disappeared. However, the graphite peak is not effected (Fig. 1c). The major changes have been noticed (Fig. 1d) at 850^{o}C calcination and quenching. The phase transformation of calcite mineral is noticed to CaO and $Ca(OH)_2$. Further it is also noticed that at this temperature the peak intensity of graphite is minimum which may be the evidence that the carbon starts burning. The acid leached sample as shown in Fig. 1e, exhibits the major mineral phases viz. graphite, quartz and kaolinite. The mineral phase of calcite totally disappeared due to dissolution.

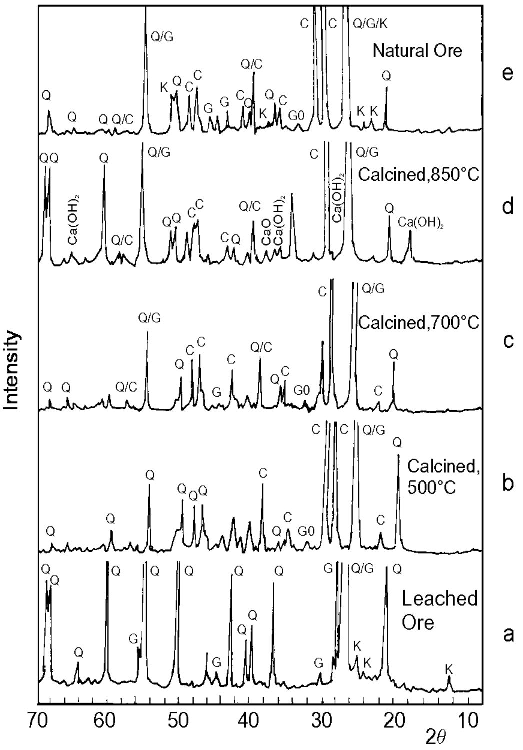

Fig. 1 X-ray diffraction pattern of different pretreated samples

From these results it is concluded that the chosen graphite ore majorly contains graphite, calcite and quartz. Stage comminution and flotation shall not alone upgrade the graphite to the desired level, as the calcite also co-floats along with the graphite. The alternate routes either calcination or acid leaching may be chosen for pretreatment of the ore prior to the processing.

It is important to mention that the presence of major or minor mineral or element at different size distribution indicates that one of the minerals is liberated [7]. Based on this assumption the XRD data were studied.

Figure 2 represents typical X-ray diffraction data of different size fractions of the graphite sample drawn on *d*-value *vs.* *I*/*I* max. Since the *d*-value of graphite and quartz are interfering with each other, assessing the liberation sizes of graphite or quartz is difficult. The *d*-value *vs.* *I*/*I* max. of calcite mineral is independent of graphite and quartz. The more intense peak for calcite is seen at above 350 and below 90 micron size fractions. The peak intensity is found minimum at size fractions between –250 +150 microns. From these observations it can be concluded that the major accumulation of calcite mineral may exist at above 350 and below 90 micron size fractions and minimum between –250 +150 microns.

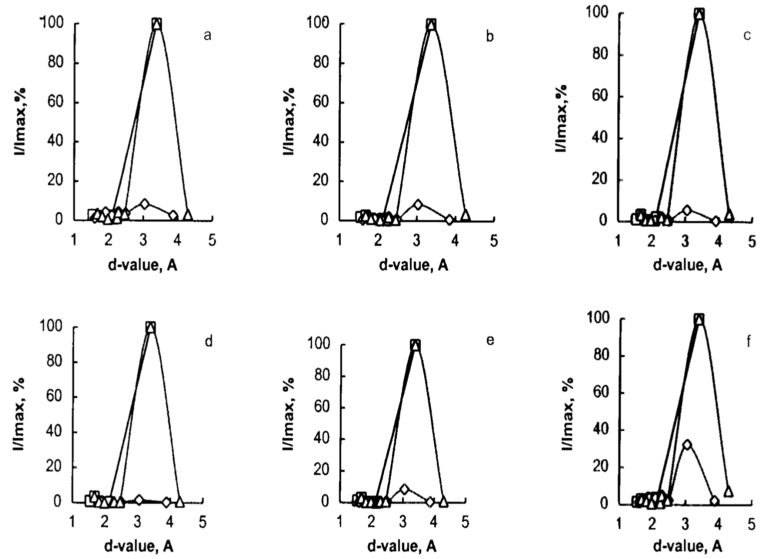

Fig. 2 XRD intensities of graphite, calcite and quartz in ore and different size fractions of graphite ore; – □ – graphite; – ◊ – calcite; – ▵ – quartz

Differential thermal analysis

The DTA curves of the different size fractions of graphite ore are presented in Fig. 3. Similarly the DTA curves of the ore and products are also shown in Fig. 4. The endothermic and exothermic peaks of different samples and the corresponding minerals identified are shown in Tables 1 and 2. The TG curves of these samples are also shown in Figs 5 and 6 respectively.

The nature of the DTA curves for all the size fractions (Fig. 3) and ore sample (Fig. 4) are quite similar. But the shift of peak temperature or peak intensity observed from sample to sample is due to variation in concentration minerals pres-ent in the samples [5, 8].

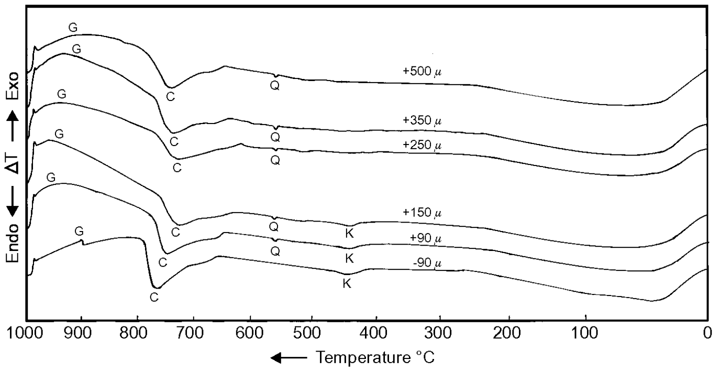

Fig. 3 DTA curves of different size fractions of graphite ore. G – graphite; C – calcite; Q – quartz; K – kaolinite

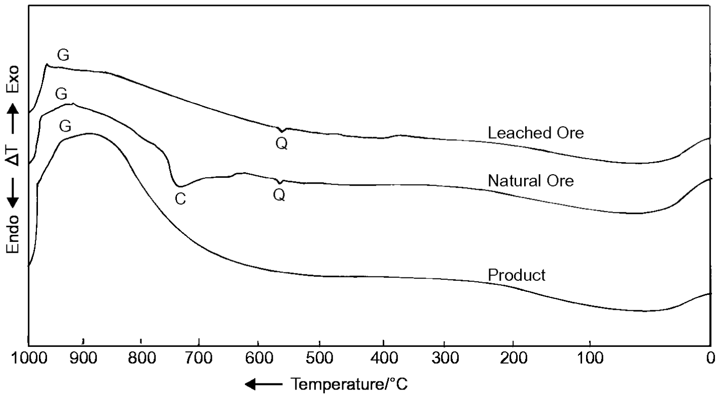

Fig. 4 DTA curves of ore, leached ore and product (graphite ore). G – graphite; C – calcite; Q – quartz

Table 1 Identification of minerals present in different sizes of graphite ore sample by DTA/TG studies

Size microns	Peak$_{\text{exo}}$/°C		Peak$_{\text{endo}}$/°C		Minerals identified
	T_{range}	T_{peak}	T_{range}	T_{peak}	
+500	600–665	645	559–561	560	quartz
	805–970	905	666–765	457	calcite
	989–991	990			graphite
+350	600–660	640	559–561	560	quartz
	860–980	935	660–750	735	calcite
	989–991	990			graphite
+250	550–640	620	564–566	565	quartz
	900–970	935	650–745	725	calcite
	984–986	985			graphite
+150	570–650	630	405–470	440	kaolinite
	930–970	960	559–565	560	quartz
	989–991	990	680–740	725	graphite, calcite
+90	525–685	640	405–490	445	kaolinite
	880–970	940	559–561	560	quartz
	984–986	985	690–760	740	graphite, calcite
–90	510–720	660	410–490	445	kaolinite
	984–986	985	720–780	765	graphite, calcite

Table 2 Identification of minerals present in natural, leached and beneficiated graphite ore samples

Sample	$\mathrm{Peak}_{\mathrm{exo}}/{}^{\mathrm{o}}\mathrm{C}$		$\mathrm{Peak}_{\mathrm{endo}}/{}^{\mathrm{o}}\mathrm{C}$		Minerals identified
	T_{range}	T_{peak}	T_{range}	T_{peak}	
Ore	600–665	640	559–561	560	quartz
	850–980	935	650–750	735	calcite
	985–991	990			graphite
Leached ore	350–420	395	564–566	565	quartz
	810–990	985			graphite
Concetrate	810–980	895			graphite

The characteristic DTA curves of kaolinite exhibit both exothermic and endothermic peaks [9, 10]. In the present sample, size fractions +150, +90 and –90 μ exhibit the endothermic region temperature range 405–490°C and the corresponding exothermic peak range 900–1000°C. However, this exothermic peak also interferes with graphite. The absence of endothermic peak in coarse size fractions +500, +350 and +250 μ indicates the absence of kaolinite.

The endothermic peak range between 560–565°C indicate the presence of quartz [8], in all the fractions above 90 micron sizes. At below 90 size fraction, this peak is insignificant, which indicate the existence of quartz is minimum compared to other size fractions.

The major exothermic peak which starts at about 510°C and terminates at around 990°C in all the samples, suggest the combustion of carbon, under the conditions of ambient air flow [5, 8]. The sudden depression of the exothermic peak in the temperature range of 650–780°C resulting in an endothermic region, points to the decomposition of calcite, $CaCO_3$, which have endothermic peak temperatures at around 725–765°C. The intensities of these peaks in the 720–780°C (Fig. 3) and 666–765°C endothermic region in corresponding to samples +500 and –90 micron size fractions as compared to other fractions indicate a higher percentage of calcite.

The DTA curves of ore and products, shown in Fig. 4 and Table 2 indicate that the ore consists of (a) quartz, endothermic peak 560, (b) calcite, endothermic peak, 735 and (c) graphite, exothermic peak 990°C. The acid treated sample consists of (a) quartz, 565 and (b) graphite, exothermic peak, 985°C. The product (concentrate) containing graphite as major mineral, as seen from the broad exothermic peak 895°C.

The TG curves of all size fractions (Fig. 5) also indicate that the thermal decomposition starts at around 650 and ends at about 990°C. The steepness in the mass loss curve observed between 700–850°C suggests that the decomposition of calcite is maximum. The mass loss curve between 800–850°C is observed maximum between two size fractions i.e. +500 and –90 μ. This is due to the presence of high amount of calcite, which decomposes simultaneously with burning of graphite carbon. The trend is similar in other size fractions but not significant.

The TG curves of ore (Fig. 6) is similar with above size fractions, while the TG curves of products shown dissimilarity with ore due to absence of calcite. The data indicate that the significant mass loss noticed from 750 and steepens down from 850

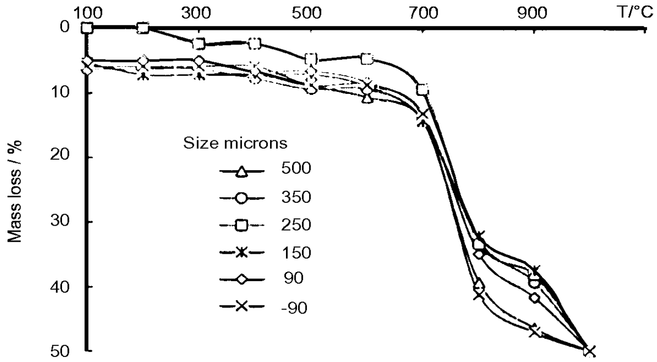

Fig. 5 TG curves of different size fractions of graphite ore

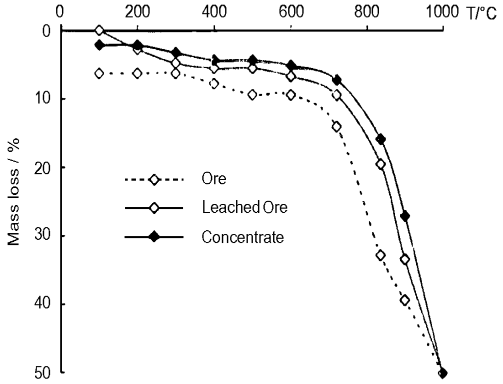

Fig. 6 TG curves for graphite ore and products

Table 3 Estimation of minerals present in the ore by DTA/TG analysis

Size/ μ	Mass/	Calcite/	Graphite/	Silicates/
	%			
+500	16.9	39.1	18.5	42.4
+350	27.7	34.1	21.0	44.9
+250	20.6	29.1	22.9	48.0
+150	24.1	27.1	28.6	44.3
+90	5.3	40.1	19.1	40.8
–90	5.4	60.1	10.4	29.5
Total	100.0	33.9	22.2	43.9

to around 1000°C. This mass loss is the characteristics of combustion of graphite carbon between 850–980°C. All these observations are in agreement with other researchers studied on various ores [5, 8].

A reasonable semi-quantitative estimation of the minerals present is possible by integrating X-ray, thermal and chemical analytical data [10]. The mass loss gives directly the proportion of gas (CO_2) evolved from the material. Quantitative estimation of graphite, is possible if the loss in mass in the temperature range 750–990°C is considered due to decomposition of calcite and combustion of graphite carbon. In the present work, the quantity of calcite mineral was calculated by analyzing the CaO content from each size fractions. The theoretical amount of CO_2 evolved was calculated from the ratios of molecular mass of calcite, $CaCO_3$ to that of CO_2 gas.

The quantity of graphite mineral was calculated from the difference of mass loss due to CO_2 evolved by $CaCO_3$ to that of total mass loss due to CO_2 evolved from calcite and graphite minerals. The relative mineral distributions were calculated in each size fraction for calcite, graphite and silicates (mostly quartz) and total composition of minerals present in the ore are shown in Table 3. This data indicate that the ore consists of 30–35% calcite, 20–25% graphite and 40–45% silicate minerals. These observations are found similar with the microscopic studies [6]. Further the data also reveal that the calcite liberates at below 90 micron size fraction and accounting for 60% calcite and 10% graphite minerals distribution. Hence to obtain calcite free graphite, the ore needs be calcined at around 850°C temperature and ground to below 90 micron size for ore processing.

Conclusions

The experimental data obtained from DTA/TG, XRD and chemical analysis on low grade calcareous graphite ore for assessing its implications in beneficiation process reveal that the ore consists of 30–35% calcite, 20–25% graphite and 40–45% silicate minerals. Calcite is significantly liberated below 90 micron size and contains 60% calcite and 10% graphite. On calcination kaolinite disappears at 500 and calcite decomposes between 700–850°C. Graphite starts combustion at 850°C. Hence to obtain calcite free graphite by flotation, the ore needs to be calcined below 850°C and ground to d_{80} passing size 75 micron.

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