

ACHIEVEMENTS IN BENEFICIATION AND PROCESSING OF LOW GRADE GRAPHITE DEPOSITS, EGYPT

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Beneficiation of low graphite deposits sampled for Barramiya, Bent Abu Garriya and Wadi Sitra was carried out through systematic flotation experiments using a mixture of (2-ethyl hexanol and hydrocarbon oil) as a collector in addition to several cationic and anionic co-collectors added to the collector mixture to improve flotation rate. It appears that flotation rate could be increased when ethoxylated sulfonate used as anionic co-collector as well as when the selectivity of graphite concentrate is increased. Processing of graphite concentrate which was carried out through roasting with sodium hydroxide and leaching with hydrochloric acid led to production of concentrate analyzing 92% fixed carbon which meets the raw material standard for the manufacture of carbon electrode and electrochemical cells.

Key words. Beneficiation, Processing, Low grade graphite.

Introduction

Graphite is one of the most versatile of non metallic minerals because of its diversified properties. It is unctuous, marks readily, burns slowly, almost chemically inert, flexible over a large temperature and a good conductor of heat and electricity. Graphite is also hydrophobic, has a negative temperature coefficient of resistivity, has excellent weathering properties, tends to emulsify with water in oil, readily soluble in molten iron and after oxidative treatment and can exfoliate like vermiculite [1-4]. These properties give rise of its major uses in lubrication, refractories, marking instruments, electronic products and paints [3].

Graphite occurs primarily as a product of metamorphism of carbonaceous rocks and occurs as three physical distinct forms namely disseminated flakes, veins (as crystalline or plumbago) and amorphous [4].

Beneficiation and upgrading of graphite is carried out through crushing, grinding, wet tabling and flotation. At present, flotation is considered as an adequate method for upgrading of low grade graphite deposit [5-9]. Processing of graphite flotation concentrate is applied to produce high pure concentrate which can not be obtained by flotation. Processing of graphite was carried out through acid leaching (HCl, H₂SO₄ and HF) [9] to remove medium and low quality carbon.

Graphite recorded in different localities in Egypt, in the Barramiya area, at Bent Abu Gerriya and at Wadi Sitra, occurs as thin seams of graphite schist associated mostly with serpentinites [10-11].

In studied areas, the graphite occurs as fine grained flakes and clusters of flakes in pelitic schist. Many flakes are rimmed and partially or wholly replaced by calcite. Graphite and graphite-calcite composite grains are also found as inclusions

in arsenopyrite in mineralized schist and serpentinites: The graphite bearing country rocks are greenish-white, fine grained and massive. They consist of several mineral assemblages namely 1) Talc-serpentine (mainly antigorite) - Chlorite and carbonates (dolomite or magnesite 2). Talc-antigorite - dolomite - quartz. 3) dolomite - antigorite - epidot and 4) Talc - tremolite - little antigorite - anthophyllite.

The present study deals with upgrading some of the low grade graphite deposits sampled from (1) Barramiya, (2) Bent Abu Garriya and (3) Wadi Sitra by using flotation as an effective separation method. The reagent scheme employed includes the use of a collector (mixture of 60% 2-ethyl hexanol and 40% hydrocarbon oil), in addition to the use of some cationic and anionic co-collectors to improve flotation rate and selectivity of graphite. Another important feature of the current study is the processing of graphite flotation concentrate through a) fusion with sodium hydroxide and b) leaching with HCl. Work described in this paper summarizes the results obtained from the optimization study.

Materials and Methods

Low grade graphite deposits were sampled from Barramiya, Bent Abu Garriya and Wadi Sitra. Graphite samples were deslimed and screened using 710 and 200 microns screens. The undersize material were discarded while the oversize fraction was ground followed by desliming and screening and passed through a 200 micron screen. Chemical analyses of the graphite samples are given in Table 1.

Reagents. i) Collector: A mixture of 60% 2-ethyl hexanol and 40% hydrocarbon oil. ii) Co-collectors: Cationic (ammonium sulfate) Anionic (ethoxylated sulfonate). iii) Frothing: Pine oil. iv) Depressor: Sodium silicate. v) Other reagents.

TABLE 1. CHEMICAL COMPOSITION OF GRAPHITE DEPOSITS (2-200 μm).

Location	Barramiya	Bent Abu Garriya	Wadi Sitra
Content	G1	G2	G3
Ash	87.4	92.2	91.0
C(%)	6.3	2.7	4.1
H(%)	0.5	0.8	0.6
N(%)	0.06	0.04	0.04
S(%)	0.05	0.1	0.09
O(%)	5.8	4.02	4.2

*Determined by difference.

Nitric acid and potassium hydroxide used as pH modifying flotation.

Apparatus. Laboratory flotation tests were carried out using a Denver (Model D-I) flotation machine with 69 cm. diameter impeller and 1.5 litre cell. An agitation intensity of 1500 rpm was maintained during conditioning and flotation. Fusion of graphite flotation concentrate was conducted in an electrically heated muffle furnace. Leaching experiments were performed in 500 ml. round bottom flask placed in a thermostatically controlled oil bath.

Procedure. a) *Flotation:* Two hundred grams of graphite were conditioned at the desired pulp density for 30 minutes after which water was added in order to maintain a graphite concentration of 140 g/l during flotation. All experiments were carried out using tap water, and flotation was continued until completion. Three different graphite deposits which are representative of studied areas were used namely G1 (Barramiya), G2 (Bent Abu Garriya) and G3 Wadi Sitra. (b) *Fusion and leaching:* The produced graphite flotation concentrate was washed, dried, ground 100% < 200 μm and thoroughly mixed with commercial grade sodium hydroxide, spread evenly in nickel boat to a depth of 3 mm. and heated in a muffle furnace for a temperature (800-900°C and 60 minutes. The door of the muffle was left open to allow for excess of oxygen. The charge of 10g. while still hot was tipped and dissolved by stirring hydrochloric acid with known concentration and temperature for a specified time. The graphite concentrate was removed from the hydrochloric acid solution by filtration and the residue is then analyzed for carbon content.

Results and Discussion

The effects of amount of collector and co-collectors used, and the time of flotation on graphite recovery for the three studied graphite deposits G1, G2 and G3 are illustrated in Fig. 1-3. The recovery of graphite is dependent on the ash content in the studied graphite deposits. It is indicated that

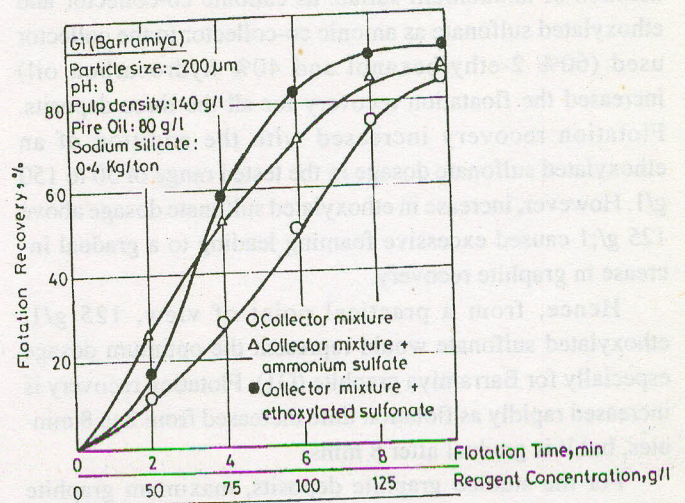


Fig. 1. Effect of flotation time and reagent concentration on graphite flotation recovery.

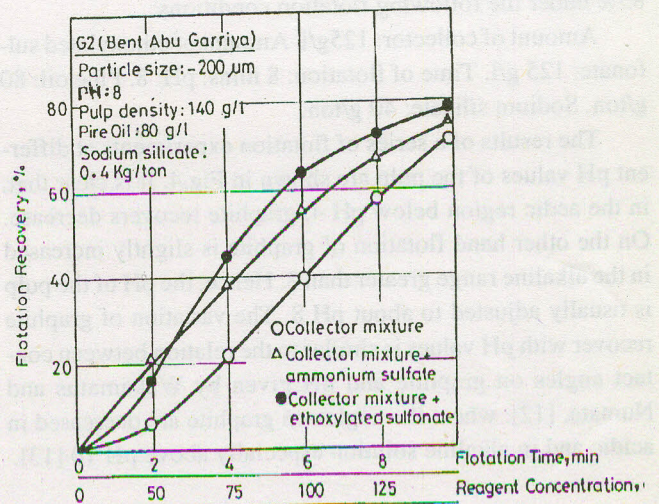


Fig. 2. Effect of flotation time and reagent concentration on graphite flotation recovery.

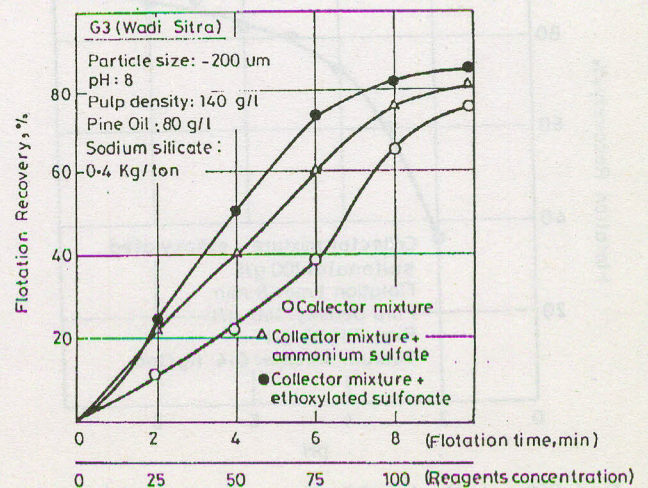


Fig. 3. Effect of flotation time and reagent concentration on graphite flotation recovery.

addition of ammonium sulfate as cationic co-collector and ethoxylated sulfonate as anionic co-collector to the collector used (60% 2-ethylhexanol and 40% hydrocarbon oil) increased the flotation recovery for all the three deposits. Flotation recovery increased with the addition of an ethoxylated sulfonate dosage in the tested range of 50 to 150 g/l. However, increase in ethoxylated sulfonate dosage above 125 g/l caused excessive foaming leading to a gradual increase in graphite recovery.

Hence, from a practical point of view, 125 g/l ethoxylated sulfonate would represent the optimum dosage especially for Barramiya graphite (G1). Flotation recovery is increased rapidly as flotation time increased from 2 to 8 minutes, but it is gradual after 8 mins.

For the studied graphite deposits, maximum graphite recover is 90% for Barramiya graphite deposit (G1), 78% for Bent Abu Garriya (G2) and for Wadi Sitra graphite (G3) is 85% under the following flotation conditions:

Amount of collector: 125g/l. Amount of ethoxylated sulfonate: 125 g/l. Time of flotation: 8 mins. pH: 8. Pine oil: 80 g/ton. Sodium silicate: 40 g/ton.

The results of a series of flotation experiments at different pH values of the pulp are shown in Fig.4. It is clear that, in the acidic region below pH 4, graphite recovers decrease. On the other hand flotation of graphite is slightly increased in the alkaline range greater than 8. Hence, the pH of the pulp is usually adjusted to about pH 8. The variation of graphite recover with pH values is similar to the relation between contact angles on graphite and pH given by Wakamatus and Numata, [12]. where the angles on graphite are decreased in acidic and in alkaline solution especially above pH 10 [13].

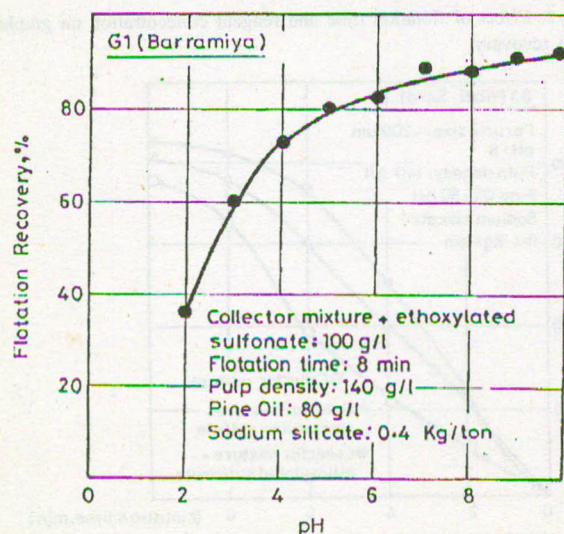


Fig.4. Effect of pH value of flotation medium on graphite flotation recovery.

The influence of sodium silicate as effective depressor of different gangue minerals associated with graphite was studied by carrying out experiments in different amounts of sodium silicate ranging from 0.2 to 1.0 kg/ton. As shown in Fig. 5, flotation of graphite is remarkably decreased as the amount of sodium silicate increased from 0.6 to 1 kg/ton. Literature data of (Klassen and Patobilskaya0, [14] and

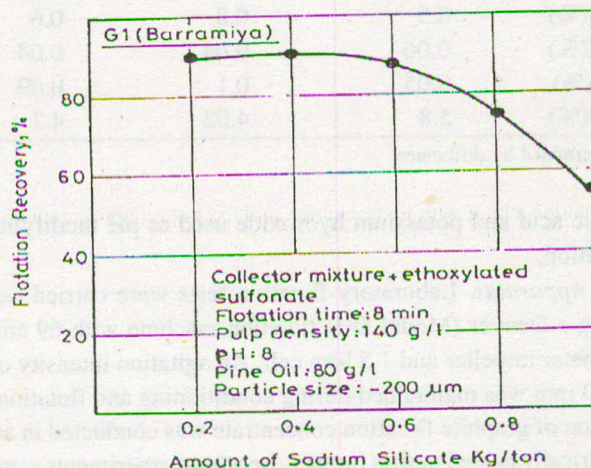


Fig.5. Effect of sodium silicate on graphite flotation recovery.

Plaksin, [15] show that the depression action of sodium silicate is connected with the hydrolysis of sodium silicate in the pulp with the formation of silicic acid and sodium hydroxide.

The flotation treatment produced a graphite concentrate assaying 80.6% carbon especially for Barramiya graphite deposit (6.3% carbon), while for Bent Abu Garriya (2.7% carbon) and Wadi Sitra (4.1% carbon) the obtained graphite concentrates assay 69.4% carbon and 74.2% carbon respectively. It is very difficult to upgrade further by flotation alone. For high purity product, the graphite concentrate must be purified by chemical processing.

Chemical purification of produced graphite concentrate. Chemical purification of produced Bent Abu Garriya graphite concentrate was carried out by: Fusion with sodium hydroxide followed by Hydrochloric acid leaching.

Extensive numbers of fusion and leaching processes were carried out to reach the optimum parameters with highest carbon content. The parameters studied for fusion are: Temperature. Duration time and Amount of added sodium hydroxide.

Figure 6. shows that, it is generally found that fusion at temperature up to 600°C has only a little effect on graphite purification while fusion above 900°C resulted in marked decline in fixed carbon content at fusion time range (20-60 min.).

As indicated from Fig.7. the amount of added sodium hydroxide was chosen to be in the range of (20-30%) at both

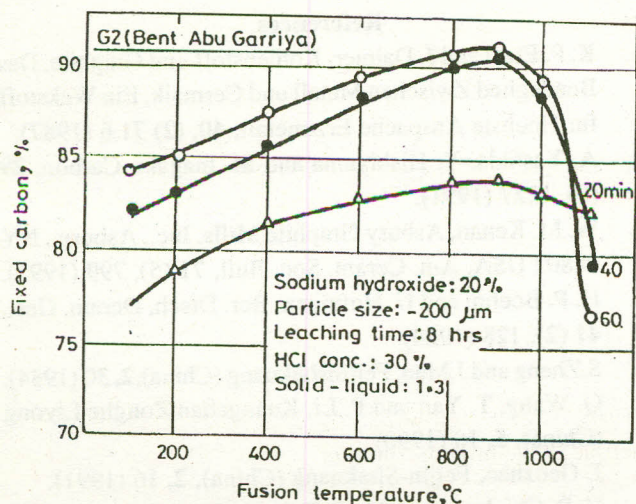


Fig. 6. Effect of fusion temperature and time on carbon content of graphite.

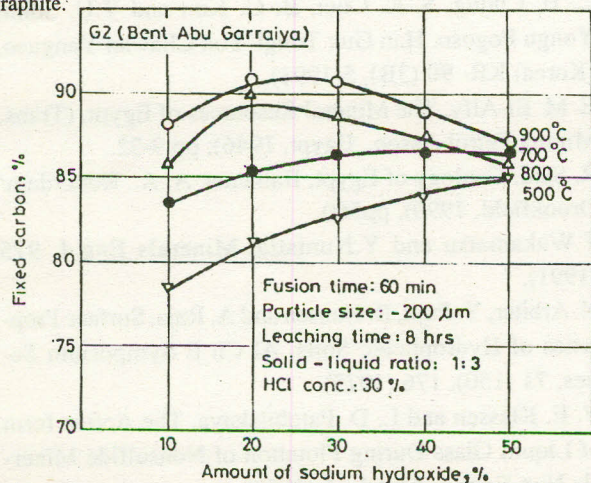


Fig. 7. Effect of amount of sodium hydroxide on carbon content of graphite.

800° and 900°C, while at 500° and 700°C, increasing of addition of sodium hydroxide led to a remarkable increase in fixed carbon content.

A series of leaching experiments was carried out in the temperature range of 40-90°C to study the effects of temperature and hydrochloric acid concentration on purification of Bent Abu Garriya graphite concentrate. It is worthy to mention that, leaching experiments were carried out under the following conditions: Leaching time: 2-10 hrs. Solid-liquid ratio: 3:1 Acid concentration: 10-40% Particles size: 100%-200μm.

The obtained results are graphically represented in Figures 8 and 9. These results reveal that the fixed carbon content increases with the increase of temperature and time. The maximum carbon content of 95% is reached at 90°C after 8 hrs (Fig. 8). The effect of acid concentration on graphite pu-

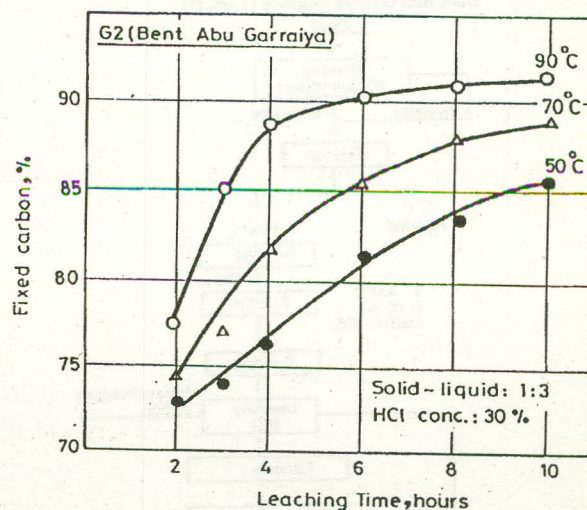


Fig. 8. Effect of leaching time and temperature on carbon content of graphite.

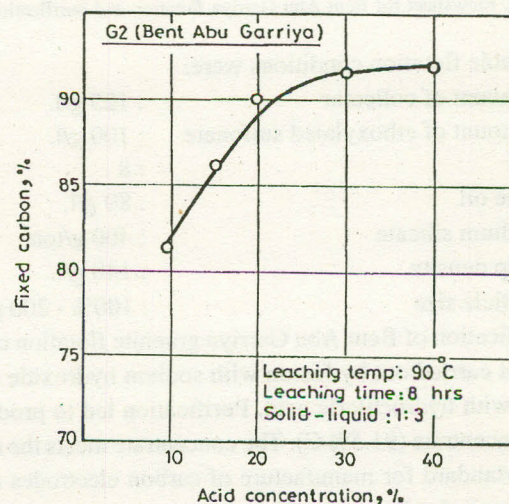


Fig. 9. Effect of HCl concentration on carbon content of graphite.

rification is clearly illustrated in Fig. 9. where the increase of acid concentration from 10 to 30% led to a remarkable increase in carbon content, while further increase of acid concentration (> 30%) has practically no significant effect on graphite purification.

Conclusion

Beneficiation of some Egyptian low grade graphite deposits from Barramiya, Bent Abu Garriya and Wadi Sitra was carried out through flotation by using a mixture of 2-ethyl hexanol and hydrocarbon oil as a collector in addition to co-collectors of cationic and anionic types.

Maximum flotation recovery of the studied graphite deposits was as follow: For Barramiya (6.3% C) is 90% & Bent Abu Garriya (2.7% C) is 78% and Wadi Sitra (4.1% C) is 85%.

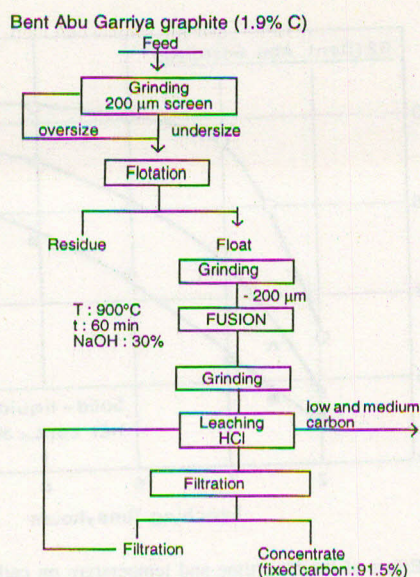


Fig.10. Flowsheet for Bent Abu Garriya flotation and purification.

Suitable flotation conditions were:

- Amount of collector : 125 g/l.
- Amount of ethoxylated sulfonate : 100 g/l.
- pH : 8
- Pine oil : 80 g/l.
- Sodium silicate : 400 g/ton.
- Pulp density : 140 g/l.
- Particle size : 100% - 200 µm.

Purification of Bent Abu Garriya graphite flotation concentrate is carried out by fusion with sodium hydroxide and leaching with hydrochloric acid. Purification led to production of concentrate (91.5% C). The concentrate meets the raw material standard for manufacture of carbon electrodes and electrochemical cells.

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