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Recovery of Flake Graphite from Kish

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Abstract. A laboratory investigation was made to recover high quality flake graphite from the steel making waste. The waste, which is called Kish, initially contained 65% graphitic carbon. Acid leaching technique was employed to purify the waste and it was completed in two steps using HCl and HF. This paper deals with the results on the optimization of leaching parameters like acid concentration, liquid to solid ratio, time and temperature. First leaching with HCl upgraded the Kish to 92.48% @ 99.74% recovery, while second leaching with HF further improved the grade up to 99.38% @ recovery 99.89%.

Keywords: flake graphite, acid leaching, Kish, steel waste

Introduction

Graphite is a naturally occurring form of carbon with a unique combination of properties that makes it important for a very wide range of industrial and consumer applications. It is a soft mineral, also known by the names of black lead, plumbago and mineral carbon. The word graphite is derived from Greek word "graphein", to write. It has a Mohs hardness of 1 to 2 and exhibits a perfect basal cleavage. Depending upon the purity, the specific gravity is 2.1 to 2.3. The theoretical density is 2.26 g/cm^3. It is grey to black in colour, opaque, has a metallic luster, is flexible but not elastic. It has high thermal and electrical conductivity, is highly refractory, chemically inert and has a high melting point of 3500 °C. Its low coefficient of friction makes it suitable for use as a high temperature lubricant, as a component in foundry facings, and as an ingredient in paints. It has high electrical conductivity, which is essential for use in the manufacture of carbon brushes for electric motors and batteries (Anwar *et al.*, 2006; Khan *et al.*, 2003; Kalyoncu, 2001; Gordon, 1995).

Generally, two types of graphite, natural and synthetic, are encountered. Natural graphite is classified into three types: flake, crystalline, and amorphous. Flake graphite consists of isolated, flat, plate like particles with angular, rounded or irregular edges. Flakes can be homogeneously distributed throughout the ore body or in concentrated lens-shaped pockets. Crystalline graphite is found in veins of solid graphitic carbon with a massive structure composed of needle like inter-growth crystals with the long axis perpendicular to the enclosing wall rock. In some instances, it is found adjacent to flake graphite. However, in industry, crystalline graphite and flake graphite are synonymous terms for material of high graphite content, as distinguished from amorphous. The term amorphous, however, is a misnomer because this material is very crystalline. It is a massive form of graphite with a microcrystalline structure. Its crystallographic structure can only be observed by using X-ray diffraction methods. Amorphous graphite typically contains higher ash content than other forms of natural graphite (Brady, 2004; Liu, 2003; Kalyoncu, 2001; Gordon, 1995; Ahmed and Siddiqi, 1993).

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According to Brady (2004), natural high-grade graphite can be divided into two forms: foliated and amorphous. Foliated graphite is used principally in manufacture of crucible and lubricants, and amorphous, in that of lead pencils, foundry facings, carbon brushes, molded parts and paint pigments. For core assemblies in nuclear reactors, graphite of ultra pure quality is essential (Bhima and Patnaik, 2005).

Synthetic graphite is classified into three types: primary or electrographite, secondary, and graphite fibres. Primary graphite is essentially pure carbon produced from petroleum coke in electric furnaces and is used mainly in the manufacture of electrodes and electric carbon brushes. Secondary synthetic graphite more closely resembles the natural graphite in terms of purity, but has a lower density, higher electric resistance, and higher porosity. Graphite fibres are used mostly in the manufacture of aerospace and sporting goods (Kalyoncu, 2001; Gordon, 1995).

Graphite is marketed in grades by purity and fineness. Number one flake contains at least 90% graphitic carbon (Kalyoncu, 2001; Crossley and Peter, 1999). Generally prices of flake graphite concentrates are higher than those of amorphous or microcrystalline graphite (Kalyoncu, 2001; Gordon, 1995). As with all natural minerals, the availability of graphite is diminishing and costs are rising. Furthermore, Pakistan is totally dependent on foreign sources for this vital material (Bhatti *et al.*, 2006).

It is very important to note that this valuable commodity is generated as a by-product in the steel industry. In the steel making process, molten iron tapped from the blast furnace contains dissolved carbon at a saturation concentration of about 6%. The liquid iron cools somewhat as it is transported and purified before entering the steelmaking furnace. On cooling, the iron cannot hold as much carbon in solution, and some of it comes out in the form of graphite flakes. Part of the graphite burns away, but much of it wafts throughout the steel plant, where it falls as a continuous rain. More graphite is skimmed from the surface of the molten iron just before it is poured into the steel furnace. This graphite material, which is called Kish has been swept, vacuumed, and shoveled from steel plants and buried as a valueless waste, for decades, although it appears to be equal to, and for some uses, better than natural graphite (Kalyoncu, 2001; Gordon, 1995; Nicks, 1993).

When graphite of 99% or better purity is required, chemical methods must be used to purify the Kish material. The most efficient one involves the use of gaseous chlorine, fluorine or halogenated hydrocarbons at high temperatures (600-2800 °C), or repeated digestion and washing with HCl and HF. The US Bureau of Mines has demonstrated a new processing method to produce high quality flake graphite from Kish. This process is easy and consists of acid leaching to remove the contaminants (Laverty *et al.*, 1994).

In this study steel waste namely Kish was obtained from Pakistan Steel, Karachi, and acid leaching technique was employed to purify it. This paper presents the results on the optimization of acid leaching parameters like acid concentration, liquid to solid ratio, time and temperature.

Materials and Methods

The representative sample of Kish from Pakistan Steel, Karachi, was subjected to coning and quartering and refill was also used to prepare the head sample for chemical analysis. For chemical analysis, conventional laboratory techniques of volumetric and gravimetric analysis were employed. Complete chemical analysis of Kish is presented in Table 1. Kish was also subjected to X-ray diffraction for phase determination. For this purpose, Diffractometer D-5000 (Siemens, Germany) was used. The diffraction pattern of Kish is presented in Fig. 1.

A series of batch tests was conducted on Kish to study the leaching effect and to determine the optimum leaching conditions. In these tests Kish (0.005 to 5.0 kg per batch) was leached in two steps using HCl and HF. The pulp was stirred manually from time to time with the help of a glass rod. The leaching results are presented in Fig. 2 (a, b, c, d) and Fig. 3 (a, b, c, d).

Results and Discussion

The grade (graphitic carbon 65%) of Kish waste, presented in Table 1, seems to be more than sufficient to produce the high quality flake graphite concentrate despite presence of other impurities (Nicks, 1993). Fig. 1 indicates that Kish mainly contains flaky graphite, so acid leaching can be considered the proper route for its beneficiation (Graham, 1994). The X-ray diffraction pattern presented in Fig. 1 was verified by using the JCP.CAT programme provided with the X-ray Diffractometer D-5000 (Siemens, Germany). This programme contains D/I values of about 60,000 Standards for material identification (Mannan *et al.*, 2006).

It is evident from Fig. 2 and 3 that the first leaching with HCl upgraded the Kish to 92.48% @ 99.74% recovery, while second leaching with HF further improved the grade up to 99.38% @ 99.89% recovery.

Fig. 2a shows the effect of HCl concentration on the purification of Kish. It is seen that under similar conditions of leaching, the grade of graphite increases with the increase in HCl concentration. At 5g/l HCl, grade reaches 92.48% @ recovery of 99.89% after which it becomes constant.

Table 1. Chemical analysis of Kish

Constituents	Percentage (%)
Graphitic Carbon	65.0
SiO_2	5.40
Fe_2O_3	26.0
Al_2O_3	0.03
CaO	2.50
MgO	0.02
Na_2O	1.0
K_2O	0.05

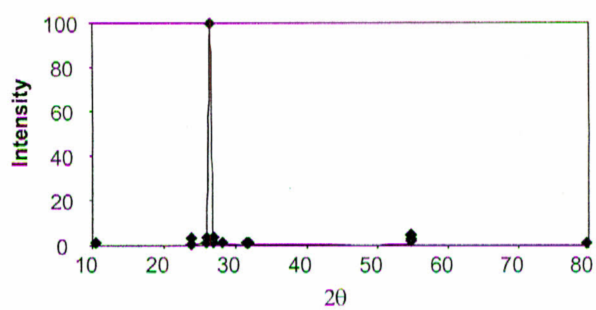

Fig. 1. X-ray diffraction pattern of Kish.

Fig. 2b shows the effect of liquid to solid ratio on the purification of Kish. It is seen that at a liquid to solid ratio 7.5, grade is 92.45% @ recovery of 99% and at 9.09 the grade is slightly higher i.e., 92.48% @ recovery of 99.74% after which it becomes constant.

Fig. 2c and Fig. 2d show the leaching of Kish as a function of time and temperature keeping the acid concentration at 5 g/l and liquid to solid ratio at 9.09. It is seen that optimum result is not achieved below 100 °C. However it may be pointed out that leaching for 3 h is required for the optimum result. It was also observed that agitation of the solution during leaching greatly helped the process. Due to formation of metal chlorides, total impurities other than silica were removed by leaching with HCl.

For removal of silica, further leaching with HF was necessary. It has been shown in Fig. 3(a, b, c, d), that purity up to 99.38%

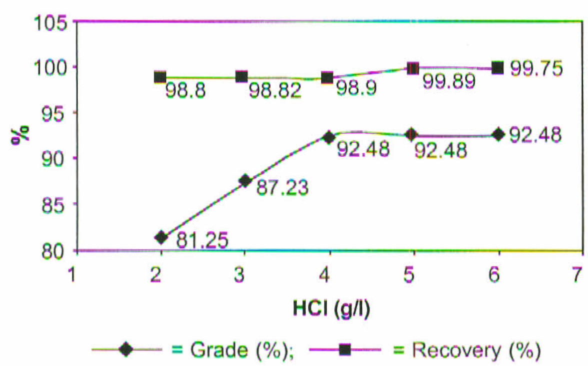

Fig. 2a. Effect of acid concentration (HCl).

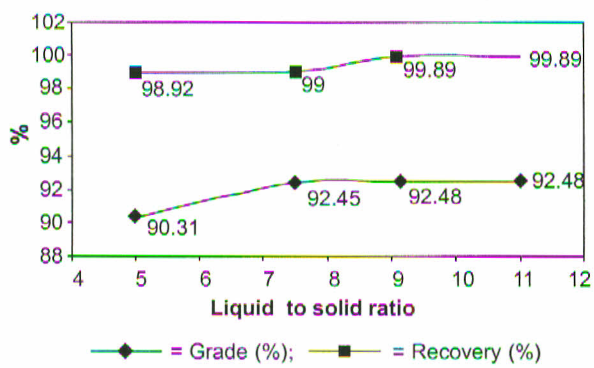

Fig. 2b. Effect of liquid to solid ratio (HCl).

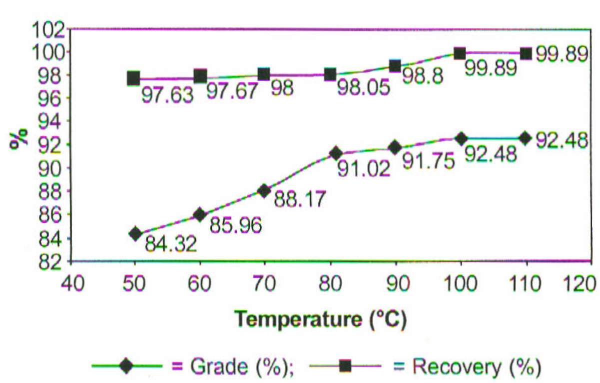

Fig. 2c. Effect of temperature (HCl).

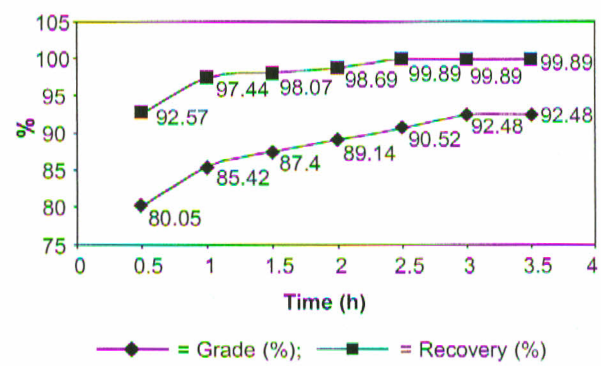

Fig. 2d. Effect of time (HCl).

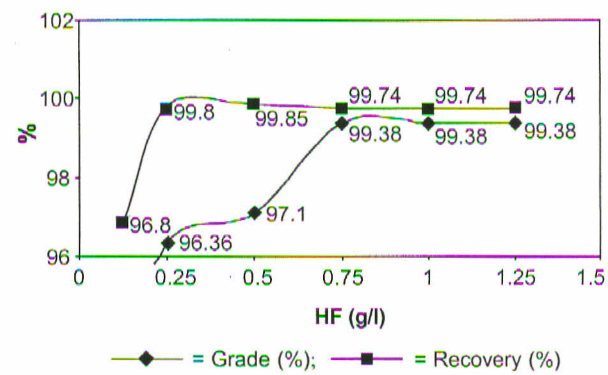

Fig. 3a. Effect of acid concentration (HF).

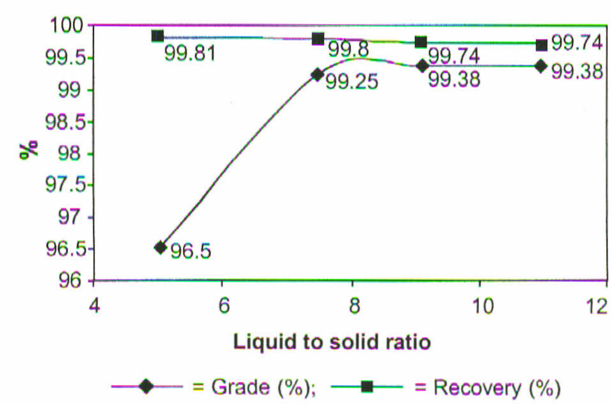

Fig. 3b. Effect of liquid to solid ratio (HF).

with 99.89% recovery is achieved, at HF concentration of 0.75 g/l with a liquid to solid ratio of one in 2.5 h. It was noted that heating the solution up to 100 °C in the water bath greatly helped the removal of silica because due to reaction with HF, it gets removed as SiF_4 vapours. It is clear from Fig. 3(a, b, c, d) that further increase in acid concentration, liquid to solid ratio or time neither improves nor disturbs the grade and recovery of the concentrate.

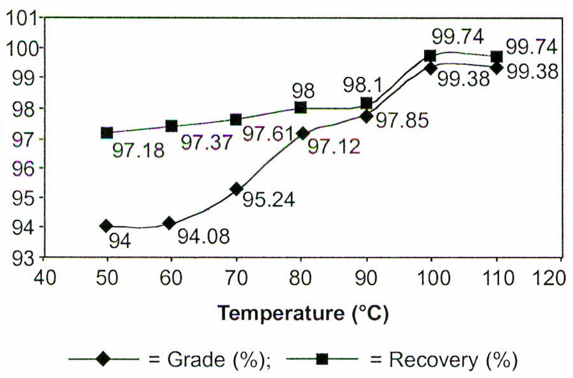

Fig. 3c. Effect of temperature (HF).

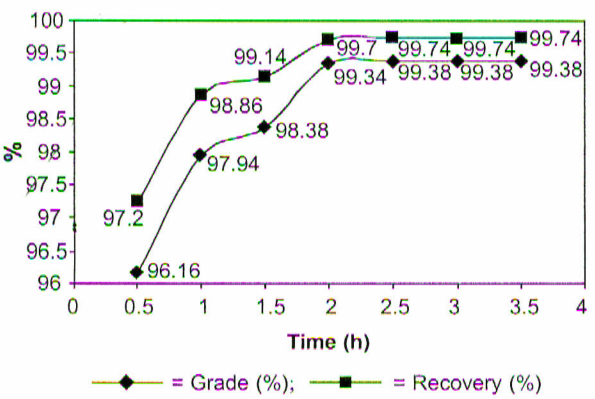

Fig. 3d. Effect of time (HF).

Conclusion

The reported experimental results lead to the conclusion that it is possible to produce high quality flake graphite concentrate (C = 99.38%) from Kish obtained from steel making waste of Pakistan Steel, Karachi. Moreover, X-ray diffraction phase analysis (Fig. 1) reveals that Kish mainly contains flake graphite, silica and iron as magnetite which do not have any complexity, restricting their separation.

However, it is recommended that detailed study on large scale may be carried out on Kish to treat it as an ore and to produce a range of graphite products competitive with the natural mineral.

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