CHAPTER II

BACKGROUND INFORMATION

History of Graphite

Graphite has been recorded from the prehistoric burial places and also from the ancient graves, though its use was probably limited to decorative purposes. Graphite first came into general use many centuries later. It was first used in the Middle Ages as a drawing material. Graphite was often confused with other minerals, such as molybdenite and artificial products used as drawing or writing material. The true nature and the identity of graphite were not recognized until the end of 18th century. In the 18th century, it was variously known as plumbago, molybdaene, blyertz or black-lead. There was much confusion among the early chemists and mineralogists over the identity of this mineral and various substances were investigated and described under the same name. The general belief was that graphite contained lead and hence the names as "black lead" and "plumbago" were given.

Agricola (1495-1550) has recorded the general use of refractory crucible made of graphite by the alchemists in their attempts to transform the base-metals into gold.

In the early 15th century, Clay-graphite crucibles were also manufactured in England.

Gasner (1565), in his treaties on the nature of minerals and rocks, has mentioned that writing pencil was composed of "English antimony".

The name graphite was given by Werner (1789) and comes from the Greek word "Graphein" meaning "to write".

Until 1820-1830 the graphite deposits of Ceylon were not exploited. After 1830, industries started using graphite and realised its commercial importance. Ceylon was the main producer of graphite for many years. At present graphite is in great demand, as a result of the growth of metallurgical industries and resulting demand for refractary materials, From early days of the industry upto 1901, Great Britain consumed more Ceylon graphite than any other country. Since 1901, U.S. and Great Britain have consumed the maximum graphite. Graphite supplies for the crucible trade at the time of the outbreak of the war (1915) was estimated to consume probably 75 percent of the World's output of graphite.

World Occurrences

On a worldwide basis, the mode of occurrence of the economic deposits of graphite is as follows:

1. Disseminated flaky graphite in metamorphosed silica-rich sedimentary rocks, such as quartz-mica schist, feldspathic micaceous quartzites or gneisses. The graphite flakes are oriented parallel to the plane of foliation. The flakes may vary in size from a fraction of a mm to an average size of about 4 mm. The principal deposits occur as lenses or layers.

2. Deposits of microcrystalline graphite formed by the action of thermal or dynamic metamorphism or both on highly carbonaceous sediments.

3. Veins, lenses or pockets of graphite ranging in thickness from a few ins. to over 7 feet, in fissures or fractures of the country rocks.

4. Deposits formed as a result of metasomatic or hydrothermal activity on metamorphosed calcareous sediments.

5. Deposits containing 1 to 5 percent flaky graphite disseminated in marble.

Klar (1958) divided graphite occurrences into micro-crystalline dense graphites and macrocrystalline silvery - bright graphites, on the basis of crystal characteristics.

Regional distribution of graphite deposits

Australia: Graphite deposits consist of flaky graphite disseminated in schists and gneisses of Precambrian age. Deposits in Western Australia consist of 35 per cent graphite in decomposed gneiss.

Austria: Fine flaky and amorphous graphite form 50 per cent of the gneiss, schist and quartzite.

Brazil: Deposits containing 20 to 30 per cent graphite occur in gneiss and anthracitic graphite occurs in schist.

Canada: Fine grained flaky graphite is fairly common in the Precambrian limestones of the Grenville Series and in the gneiss and schist of South Eastern Ontario and South Western Quebec.

Ceylon has the World's largest known deposits of lump or vein graphite. The graphite deposits occur as seams or veins in crystalline limestone, quartzite and garnet-sillimanite gneiss. The chief mode of occurrence of graphite (Wadia, 1943) is as dissemination in crystalline rock with embedded masses, veins, lenses and pockets of graphite lying concordant with the foliation planes of the host rock. Graphite occurs also with other minerals in pegmatite dykes or quartz veins. The veins range in thickness from a few inches upto 8 ft. Graphite-filled vugs are 70 feet long and upto 10 ft X 20 feet in cross-section. The highest grade of graphite ore contains as much as 98 per cent graphite.

Czechoslovakia: The Moravian deposits almost entirely consist of amorphous graphite. The Bohemian deposits contain both flaky and amorphous graphite. In Schwcuzbach-Krumau area, graphite occurs in irregular lenticular masses of graphitic schist interbedded with other metamorphic rocks.

Germany (Federal Republic): The graphite deposits consist of disseminated flaky graphite which occurs as lenses and seams in schist and gneiss in Passau district of Bavaria. The seams containing 30 per cent graphite are interbedded with gneiss and metamorphosed limestone.

Italy: Lense shaped bodies containing 40-70 per cent finely crystalline graphite occur in gneiss and mica schist.

Korea: The amorphous and flaky graphite occur in Pre-cambrian to Triassic rocks of Central and Eastern Korea that have undergone contact or regional metamorphism. The amorphous graphite occurs as irregular bands and contorted lenses oriented parallel to the enclosing schist and phyllite. The flaky type contain 85 per cent graphite while amorphous type contain 70-90 per cent graphite.

Malagasy Republic (Madagascar) has the largest reserves of flaky graphite which occur in lenses, veins, pockets and large masses in mica schists and mica-gneiss covering an area of 500 miles in the eastern part of the island. The graphite deposits in the coastal belt consists mainly of the disseminated flake in crystalline rocks averaging about 6 per cent graphite. The individual deposits range in thickness from 10 to 100 ft. and contain upto 60 per cent graphite.

Mexico: Amorphous graphite occurring in metamorphosed quartzite and slate is mined in Sonora. The graphite is formed by the metamorphism of coal beds having a maximum thickness of 24 feet. High grade deposit averages 85 per cent graphite.

Norway: Lenses in mica-schist contain 25-30 per cent flaky graphite, 3 to 5 feet thick layers containing 10 per cent graphite occur in mica schist and quartzite.

Spain: Extensive deposits containing 7 to 11 per cent graphite are worked near Toledo.

Sweden: Amorphous graphite deposits containing upto 40 per cent graphite occur in the Lepland shale.

U.S.A. : All the three varieties of graphite deposits are mined. Flaky graphite occurs in schist and gneiss in the States of New York, Pensylvania, Alabama etc. Amorphous graphite has been worked in Michigan, Rhode Island, New Mexico etc. and vein graphite occurs at Dillon, Montona.

In East Central Alabama, graphite bands of 20 to 100 feet width occur in mica schist and in intrusive pegmatite. The average grade is 2.5 to 3.5 per cent graphite.

In the Precambrian rocks on the east side of the Adirondak mountains of New York, two beds of graphitic quartz schist 3 to 30 feet thick contain streaks, pockets and disseminated flaky graphite. The associated rocks are garnetiferous gneiss and limestone intruded by granite.

U.S.S.R. has large reserves of amorphous and crystalline graphite. The Noainskiy deposit consists of three main types - columnar graphite, laminated graphite and lead-like graphite. Vein and disseminated flaky graphite occur in nepheline syenite, gneiss, schist and crystalline limestone in the lake Baikal region.

Yugoslovia: Deposits of flaky graphite occur in quartz-mica schist of Eastern Serbia.

Graphite occurrences in India

Cullen (1846), was the first to record the occurrence of graphite in India near Trivandrum.

The important domestic sources of graphite are chiefly confined to the rocks of the Khondalite Series, which extend from Orissa down to Madras and Kerala. Sporadic occurrences are found in Archean gneisses of Bihar, Madhya Pradesh and Mysore and Aravalli suite of rocks in Gujarat and Rajasthan.

The main producing districts are Bolangir, Dhenkanal, Kalahandi, Koraput and Sambalpur in Orissa; East and West

Godavari districts and Srikakulam districts in Andhra Pradesh; Ernakulam and Trivandrum districts in Kerala; and Panchmahals and Baroda districts in Gujarat.

Andhra Pradesh: In East Godavari district, graphite occurs as veins in quartzite and garnetiferous schist. The rocks are faulted and the larger bodies of graphite are reported to occur between fault planes.

In West Godavari district a vein of practically pure graphite occurs at the contact of Khondalite and weathered granitoid gneiss. In Guntur district, a fair amount of graphite occurs in gneiss.

In Srikakulam district, flaky graphite occurs as lenses and pockets associated with biotite gneiss or schist and also in association with quartz veins traversing Khondalite. Here, the deposit is in the form of thick plates having nearly 74 per cent graphite.

In Vishakapatanam district, graphite deposit having 47 per cent graphite occurring in the form of disseminations, veins and fissure fillings, are found in Khondalite.

Bihar has disseminated flaky deposits containing 55 per cent graphite occurring as thin lenses and small pockets in schist and gneissic rocks of Palamau district.

Jammu and Kashmir have fairly large amorphous graphite deposits containing 20 to 30 per cent graphite, in phyllite and schist.

Gujarat has low grade graphite deposits occurring as lenticular bands in the biotite and amphibole-quartz schist, crystalline limestone and gneiss. In Baroda district graphite is in schist and gneiss, associated with impure crystalline limestone and quartzite, while in Panchmahals district graphite is found in phyllite schist and gneiss. The associated rocks are crystalline limestone and quartzite.

Kerala: The first recorded occurrence of graphite in India was by Cullen (1846) near Trivendrum in Kerala. In Ernakulam district graphite is found in the contact zones of pegmatite, traversing garnetiferous gneiss.

Madhya Pradesh: Bands of phyllite containing up to 30% graphite occur in Betal district. In Bastar district, flaky graphite occurs in schistose rocks.

Rajasthan: Amorphous graphite near Amba was extensively worked during the first world war. In Udaipur district, beds of graphitic schist occur in rocks of Delhi system. In Banasawara district, thin veins and stringers of graphite are exposed in Aravalli phyllite, schist and quartzite and also in highly folded mica schist and quartzite. In Pali district several small lenses and disseminated flakes of graphite occur in mica schist. In Sirohi district, graphite rich crystalline limestone has been recorded.

Orissa: In Kalahandi district the calcified garnetiferous biotite gneiss contains 40 per cent graphite. Several bands contain on an average about 65 per cent amorphous and flaky graphite. In Koraput district, small deposits in the form of lenses, veins and scaly patches contain 93 per cent graphite. In Bolangir district workable deposits of graphite occur as veins associated with pegmatite and gneiss of the Khondalite series.

Tamilnadu: In the Sivamalai area in Coimbtore district, flaky graphite occurs as a sparsely distributed component of Nepheline syenite. In Tiruchirapalli district, fine grained crystalline graphite, associated with molybdenite occurs as thin bands in granite gneiss.

Karnataka: Kyanite schist contains 15 to 20 per cent graphite flakes. In Tumkur district, thin flakes of graphite are associated with quartz-augite rock and quartz veins.

Uttar Pradesh: In Almora district segregations and pockets of graphite occur in schist.

West Bangal: In Puralia district graphite occurs as disseminated flakes in mica schist. Local concentrations of fine flakes of graphite occur in felsphathic mica schist. Small flakes of graphite are also found in biotite schist, pegmatite and phyllite.

Mining and Beneficiation

Mining

Graphite is mined by conventional underground operations or by open-cast mining depending upon the depth and structure of the deposit, the quality of graphite and the nature of the overburden.

Underground mining is generally confined to the larger occurrences of seams or layers of graphite while other deposits may be worked by open-cast operations when factors such as extensive weathering of the parent rock permit the easy removal of the ore. Where the rock is weathered to a considerable extent, open-cut operations with primitive tools are used to obtain the ore. In recent years, more modern methods of production, such as hydraulic and mechanical excavation, have been introduced.

Open-cast operations in the United States are highly mechanized. Overburden is stripped by bulldozers or scrapers, and power excavators are used to remove the graphite-bearing rock. In many countries selective mining methods are employed to eliminate contamination and unwanted gangue material. Thus, deposits on the flank or those which have the least over burden or sterile material to be removed, are usually selected. The labour should be plentiful and cheap. Mechanical appliances would demand a larger capital outlay and to justify their use it would be necessary to aim at a large output. The mining laws should be liberal and should afford every inducement and security for the investment of capital. The availability of transport is an important factor.

Beneficiation

Graphite is a natural floater. The problem of beneficiation of graphite has been studied in many countries. Several dry, wet and chemical methods of refining and concentrating graphite ores are known. Dry methods of separating graphite from gangue, include jigging, grinding and sieving, air-classification and electrostatic methods. In wet-methods, the graphite is separated by washing the ore with buddles, log washers, rack washers or wet-tables. Wet-methods are effective in separating graphite from clayey and finely dispersed impurities. The Indian Institute of Science, Bangalore (1972) claims that graphite could be purified to 90% carbon by froth flotation, irrespective of the grade of the ore. The most effective method of beneficiation is froth flotation, which is particularly well adapted for ore bodies in which graphite occurs in a finely divided state. A final refining treatment may be necessary after concentration in order to eliminate impurities included between laminae. Fine grinding by rolls and buhrstones is necessary for this treatment.

The extraction of graphite from its ores and preparation for market have always presented difficulties from both the technical and economic point of view. The mica associated with flake graphite is of the same form, hardness and toughness and behaves in much the same fashion as does graphite, at all stages of mechanical treatment, and is one of the most difficult minerals to eliminate.

The flaky graphite from disseminated deposits is difficult to concentrate without reducing its size. A number of secret processes have been evolved by different firms and countries. It is difficult to recover refined graphite from rough concentrates. This difficulty is due to the fact that fine grinding is not allowed in the case of flake graphite ore because there is every chance of reducing the grain size of the flake.

The chief impurities in natural flaky graphite are quartz, calcite, mica, feldspar, iron sulfide and silicates of calcium, magnesium and aluminium. Ores of amorphous graphite are generally poor in carbon-content. The poorer grades are difficult to beneficiate on account of the extreme fineness of the particles. Sometimes they are used without upgrading for foundry facings.

The most important principle under-lying most of the milling processes is alternate grinding and screening. The grinding pulverzies the quartz, feldspar and other brittle minerals but does not materially reduce the size of the flexible graphite flakes. The screening separates the pulverized brittle minerals from the larger flakes of graphite.

Amyl alcohol, pine oil, kerosene oil, diesel oil, cresylic acid are the commonly used reagents during rougher flotation. At the time of selection of reagents the final grade of concentration and recovery is considered. Sodium hexametaphosphate, commercially known as calgon and sodium silicate are the commonly used depressant or dispersant during cleaning and grinding respectively.

Industrial applications

Graphite is a crystalline form of carbon. All graphites are crystalline but fine grained graphite is commercially known as amorphous graphite. In ancient times, graphite was used mainly as writing material. Since then, the use of graphite has increased many fold. Graphite ranging from 25 to 100 per cent graphitic carbon is consumed in various industries. About 70 per cent of the world's total consumption of graphite is in metallurgical industries viz., crucible manufacture, foundry facings, moulds etc. Other important uses of natural graphite are in lubricants, brushes for electrical machinery, dry cell battery, electrodes and pencils. Minor uses of graphite are in the manufacture of explosives, in preventing boiler scales etc.

Quality of graphite and cost of production are the deciding factors for the use of graphite in various industries. The properties of graphite must be assessed before use because graphite containing impurities such as quartz, mica, calcite, pyrite etc., affect the life and strength of the products.

The use of graphite as an important industrial raw material is mainly due to its physical and chemical properties viz. metallic lustre, high opacity, flaky form, softness, low specific gravity, high electrical conductivity, good conductor of heat, chemical inertness, low coefficient of friction and refractoriness.

The application of graphite in the field of metallurgy is two fold, one where the graphite is used electrically to produce heat for the work, and the other where the graphite acts as a refractory to hold the work while it is undergoing heat treatment. The applications of graphite as a refractory material are based on the fact that graphite is not wetted by most molten metals and is able to withstand several thermal shocks, provided the material is truly dry. The following are the main graphite-based industries.

1. Crucible manufacture: About 70-75 per cent of the world's output of graphite is estimated to be consumed in the manufacture of crucibles used in melting metals such as steel, brass and other non-ferrous alloys. All the

three types of graphite i.e. flake, lump or chip and amorphous are used in this industry.

2. Foundry facing: Graphite is an admirable material for foundry facing. It is the material which is used to give the skin of the moulds, a smooth finish, so that casting peel freely and clearly on cooling and prevent adhesion of the moulds.

3. Brushes: The graphite generally used may be the natural flaky variety or Ceylon plumbago. Dynamo and motor commutators were formerly made of copper brushes. Such brushes have now been almost entirely superceded by carbon or graphite brushes.

4. Dry cell battery: Natural or artificial graphite may be used for this purpose. Of these either amorphous graphite or finely ground flaky graphite is applied in dry-cell manufacture. Graphite is intimately mixed with manganese-dioxide, a poor conductor of electricity to produce the desired conductivity of the cell.

5. Lubricants: Graphite is ideally suitable as a lubricating agent, because of its softness, low coefficient of friction, chemical inertness and heat resistance

maintained under most normal conditions. Graphite is used because of its ready adherence to metal surfaces even under lightest pressure, where conventional lubricating oils or greases cannot be applied.

6. Paints: To protect the surface of the metal from corrosive action of sulphurous gases, acids, alkalies etc. graphite is used as the pigment in the paint industry. There is diversity of opinion as to the most suitable kind of graphite for graphite paints and the natural amorphous, natural flake and artificial varieties are all consumed by different manufacturers.

7. Boiler scale preventor: In recent years graphite is widely used in boilers for preventing scale. The action of graphite is purely mechanical and is not affected by variations in temperatures or changes in acidity or alkalinity of the water or by heat. The graphite usually recommended for preventing boiler scale is very finely ground flake so as to ensure maximum penetration into the scale. For this purpose amorphous and artificial varities are also used.

8. Pencils: About 7 per cent of the world's total production of graphite is estimated to be consumed in the pencil industry. For the manufacturing of pencil, finely ground, earthy and amorphous graphite having about 85 per cent graphitic carbon is used.

9. Explosives: Graphite controls the burning rates of smokeless powders by coating the powder grains. Natural graphite is normally preferred but electrographite also gives satisfactory results.

10. Stove polish: An amorphous natural graphite having about 80 to 82% graphitic carbon is usually preferred.

11. Nuclear reactors: Nuclear grade material for moderators and reflectors was commercially produced from natural graphite. High purity of the material and elimination of neutron absorber elements like Boron are the prime considerations.

In recent years, natural graphite is replaced by artificial (synthetic) graphite in moderators and reflectors for atomic reactors, crucibles, moulds and dies.