CHAPTER 12.14

Graphite

Andrew Scogings and Daryl Evans

PROPERTIES

Graphite is an allotrope of carbon, characterized by a hexagonal structure, with weak bonds between the carbon layers that facilitate easy cleavage, which makes it one of the softest substances known. Graphite is gray to black, opaque, very soft, and has a low density and a metallic luster. It is flexible and exhibits both metallic and nonmetallic properties, making it suitable for diverse industrial applications. Physical properties include a specific gravity of 2.2 and Mohs hardness of 1–2. Metallic properties include thermal and electrical conductivity, whereas nonmetallic properties include chemical inertness, high thermal resistance, and lubricity.

Natural graphite occurs in several forms, described as *amorphous*, *flake*, and *vein*. Graphite may also be manufactured synthetically from carbon-bearing raw materials such as petroleum coke and tar pitch. Natural graphite products generally contain associated mineral impurities, which are referred to as *ash*. These impurities may include silicate and sulfide minerals such as quartz or pyrite in the case of flake graphite. Amorphous graphite may contain sedimentary rock impurities such as shale, sandstone, quartzite, or limestone.

USES

The major uses of graphite are in refractories, batteries, expandable graphite, brake linings, and steelmaking-foundry operations. The largest end market for graphite is in refractories, foundries, and crucibles for protective linings, shapes, or vessels used in high-temperature environments such as steel production. These markets are believed to account for around 35% of total graphite consumption, predominately consuming flake and vein graphite. Steelmaking-foundry operations use graphite as a carbon raiser, as foundry facings to facilitate the removal of an object from a mold, and for lubricating extrusion dies.

The refractories market requires a range of flake size distribution and purity, which vary according to application. For example, alumina magnesia carbon bricks may demand fine flake graphite <100 mesh, whereas magnesia carbon bricks typically use 90%–95% C graphite with a broad flake distribution –100 to +50 mesh.

Metallurgy is the second largest market for natural graphite, which is used in metal production, particularly as a recarburizer in steel and consuming mainly amorphous graphite or fine flake. This accounts for approximately 25% of total graphite output. Batteries are the third largest graphite market. Although only consuming around 13% of worldwide graphite production, it is potentially the fastest growing market. Chinese producers use –100 mesh (94% C) small flake for making spherical graphite (for battery anode applications). Solid lubricants, based mainly on amorphous graphite, consume approximately 10% of production, having been a classic use for centuries.

Both flake and amorphous graphite are used in parts and components. This wide range of products varies from motor vehicle brake pads to carbon brushes for electric motors to pencils. As a group, it is believed to consume roughly 10% of total output. Brake linings use an organic friction material impregnated with graphite, especially for heavy vehicles such as trucks. Expandable graphite is another market that is anticipated to grow, and is used in applications such as fire retardation to replace halogenated retardants, insulation, and heat transmission. These markets require large flake products generally >80 mesh. Graphite is typically specified at a minimum by particle size and carbon content (purity). There are no set industry specifications, although in countries such as China, the government has established national standards.

PRICES

The U.S. Geological Survey (USGS) has published prices for graphite imported into the United States (Olson 2017):

- Flake graphite cost $1,240/t (metric ton) in 2015, compared to $1,370 in 2012.
- Amorphous (Mexican) graphite cost $370/t in 2014, compared to $339 in 2012.
- Lump and chip (Sri Lankan) graphite cost $1,890/t in 2015, which has remained relatively constant since 2011.

Andrew Scogings, Principal Consultant, CSA Global Pty Ltd., Perth, Western Australia, Australia
Daryl Evans, Director of Metallurgy, IMO Pty Ltd., Perth, Western Australia, Australia

Flake graphite prices remained relatively steady for many years until approximately 2005, after which they climbed gradually to 2008 in tandem with increased Chinese steel production. Following the global financial crisis, prices declined in 2009 before resuming an upward trend and spiking dramatically during 2011–2012. Prices have since declined to 2008 levels because of excess production versus market demand. Amorphous graphite has shown similar trends. For example, flake graphite (>80 mesh, 94%–97% C) sold for about \$750/t up until 2004. The price increased to a peak of around \$2,500/t in 2011–2012 before falling back to \$1,000/t in 2014. Currently, the price ranges from \$750 to 850/t (Industrial Minerals 2018).

One graphite price not generally quoted is for *jumbo flake*, a term that describes flakes +35 mesh size or larger. Trade is relatively limited and probably only a few thousand metric tons per year, but likely prices may have been around \$2,000/t in 2015. Spherical graphite is another product for which prices are not widely publicized. However, according to Chinese customs data, prices for uncoated spherical product range around \$3,000/t (Scogings et al. 2015b).

GLOBAL RESOURCES

Table 1 shows the global resource of graphite and includes the top 10 countries where most of the resources are identified. The reserve numbers that are included in Table 1 are separately shown in Table 2.

Table 1 Graphite resources

Country	Identified Resources, thousand Mt: Amorphous	Identified Resources, thousand Mt: Flake	Total
China	Not applicable	360,000	360,000
Russia with Ukraine	560,000	100,000	660,000
Madagascar	—	180,000	180,000
North Korea	31,000	2,100	33,100
Mexico	13,000	2,100	15,100
India	—	14,000	14,000
Czech Republic	—	13,000	13,000
Sri Lanka	450 (crystalline vein)	8,800	9,250
United States	5,900	280	6,180
Canada	—	5,700	5,700
Other	613,650	690,000	1,303,650
Total	**1,224,000 (includes crystalline vein)**	**1,375,980**	**2,599,980**

Adapted from Robinson et al. 2017

Table 2 Graphite reserves

Country	Reserves, thousand Mt: Amorphous	Reserves, thousand Mt: Flake	Total
China	55,000	6,000	61,000
Russia with Ukraine	1,000	6,400	7,400
Mexico	3,100	106	3,206
Sri Lanka	50 (crystalline vein)	1,800	1,800
North Korea	1,000	700	1,700
Canada	—	1,500	1,500
Madagascar	—	940	940
Czech Republic	—	900	900
India	—	735	735
Zimbabwe	—	600	600
Other	320	1,639	1,639
Total	**60,470 (includes crystalline vein)**	**21,320**	**81,420**

Adapted from Robinson et al. 2017

PRODUCTION

Global natural graphite production has risen from about 100,000 t/yr in the early 1900s to approximately 1.2 Mt (million metric tons) in 2014, at a compounded annual growth of about 3% since 1950.

According to USGS data, China was the world's leading producer of natural graphite and supplied about two-thirds of the market in 2014 (~800,000 t/yr). Brazil (~80,000 t/yr), India (~170,000 t/yr), Canada, and North Korea were estimated to have collectively contributed an additional 27% of global production (Olson 2017). China's production has rapidly grown since 1998, having overtaken the rest of the world in 2000. Production quoted in India has been under discussion for some time, and it is believed that the tonnages reported are for run-of-mine (ROM), not for concentrate produced; hence India's production is probably closer to around 25,000 t/yr.

Leading non-Chinese flake graphite miners and producers include

- Graphit Kropfmühl (Germany, Mozambique [under construction], and Zimbabwe),
- Skaland Graphite (Norway),
- Imerys Graphite and Carbon (Namibia [under construction] and Canada),
- Nacional de Grafite and Grafite do Brasil (Brazil),
- Zavalivskiy Graphite (Ukraine),
- Tirupati Carbons and Chemical (India), and
- Bass Metals (Madagascar).

Nacional de Grafite is reportedly the biggest mine outside of China, producing about 70,000 t/yr of concentrate.

Heilongjiang is the leading flake graphite–producing province in China and is believed to host the largest flake graphite deposits in Asia. The two main graphite mining areas are Luobei and Jixi. Producers in Heilongjiang include Aoyu Graphite Group in the Luobei area. In the Jixi area, companies such as BTR New Energy Materials, Huanyu New Energy Technology, PuChen Graphite, and the Liumao graphite mine are operational (Scogings et al. 2015b).

Shandong is also a notable producing area and includes companies such as Qingdao Black Dragon Graphite Group and Qingdao Hensen Graphite, of which the latter produces flake graphite, micronized graphite, expandable graphite, and spherical graphite. Hunan Province is the world's leading source of amorphous graphite and is believed to produce about 200,000 t/yr (Scogings et al. 2015b).

Sri Lanka is a relatively small producer, although well known for its high-quality vein graphite. There are two significant vein graphite producers in Sri Lanka: Kahatagaha Graphite Lanka (government owned and operated) and Bogala Graphite Lanka, which is owned by Graphit Kropfmühl (Scogings et al. 2015b).

GEOLOGIC SETTINGS AND RESOURCES

Economic graphite deposits occur in three main geologic types: flake graphite disseminated in metamorphosed sedimentary rocks; amorphous graphite formed by metamorphism of coal or carbon-rich sediments; and veins or lump graphite filling fractures, fissures, and cavities in country rock. Although no reliable information is available about total world reserves of graphite ore, USGS estimates 230 Mt of world reserves, accounted for by Brazil (72 Mt), China (55 Mt), India (8 Mt), Madagascar (0.9 Mt), Mexico (3.1 Mt), and Turkey (90 Mt) (Olson 2017).

EXPLORATION

Graphite is explored for using methods such as field mapping, trenching, geophysics, drilling, assaying of the graphite content, and mineralogical and metallurgical testing. Data generated in this way, if successful, could lead to the estimation of a designated *mineral resource*. Reporting mineral resources conforming to international codes requires that they are classified according to confidence in geological and grade continuity, in addition to accounting for product specifications.

Several methods are used for drilling for graphite such as reverse circulation or diamond core drilling (DD), whereas auger drilling may occasionally be used to explore highly weathered, clayey mineralization. DD is by far the preferred method of exploration drilling for graphite, as the graphite flakes and host rock are relatively undisturbed when retrieved as core and can be used for extractive metallurgical tests.

Petrographic examination of polished thin sections is a relatively affordable and quick option to estimate the in situ graphite flake size distribution and likely liberation characteristics, as graphite may be associated with mineral impurities such as iron sulfides, quartz, feldspar, and mica. Polarized-light microscopy may be complemented by methods such as scanning electron microscopy (SEM), Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN), and mineral liberation analysis (or automated SEM).

Carbon may be present in rocks in several different forms including organic carbon, carbonate minerals, or graphitic carbon. Organic carbon and carbon in carbonate minerals, such as calcite, should be removed before assaying for total graphitic carbon (TGC). These two forms of nongraphitic carbon are typically removed from the sample by acid leaching and calcination.

TGC assays quantify the amount of graphite contained within a deposit but do not indicate the amount of graphite that may be recoverable or the purity or flake size of liberated graphite and the process required to liberate and produce a graphite concentrate. Therefore, it is necessary to evaluate representative samples of mineralization from a deposit to confirm appropriate metallurgical processes and likely product mix.

The past few years have seen intensive exploration for graphite by both private and publicly listed companies, with most exploration aimed at flake graphite deposits. Australia, Canada, Mozambique, and Tanzania were the main hot spots, with the biggest resources discovered in northern Mozambique and southern Tanzania. Other target countries have included Brazil, Madagascar, Malawi, Sweden, and the United States.

This intensive exploration has added more than 4.5 billion t to the global flake graphite mineral resource base, at grades of between approximately 2% and 25% graphite. Total contained graphite is estimated to be in excess of 400 Mt and, assuming a mining and process yield of 70%, this equates to approximately 280 Mt of product of all flake sizes.

Given anticipated market growth in battery and expandable graphite applications, there is a window of opportunity for new flake graphite supply to enter the existing market. However, given the extent of new discoveries and proposed production rates, this could yield additional production of more than 1 Mt/yr of flake graphite over the next few years. This appears to be well in excess of growth opportunities, thus many projects will likely fail to reach production.

Comparing Flake Graphite Exploration and Development Projects

Graphite exploration projects may be ranked according to factors such as deposit size, contained graphite, location (country risk) and logistics, flake size distribution, product purity, offtake agreements, and expected time frame to production. Drivers for success include having a sufficiently high-grade flake graphite deposit with low stripping ratio that is economic to mine and process to yield highest-quality marketable products. In addition, jurisdiction, logistics, time frame to production, and offtake agreements must be taken into consideration.

MINING METHODS

Flake graphite deposits are typically hosted in metamorphic rocks, such as gneiss and schist, generally have tabular or lenslike geometry, and may be mined opencut, although some high-grade flake graphite deposits are mined underground in Germany, Norway, and Zimbabwe. Most flake graphite deposits being mined opencut contain between 5% and 15% graphite, whereas underground mines have grades of around 30% graphite.

Flake graphite deposits can be between 5 and 100 m thick, extend along a strike for hundreds or thousands of meters, and dip anywhere between horizontal and vertical. Deeply weathered flake graphite deposits may offer mining and processing benefits over unweathered deposits because of ease of mining and processing the soft decomposed ore. Deeply weathered deposits have been mined for many years in Madagascar and Brazil and have also been discovered in Malawi.

Vein deposits have complex geometry, are generally narrow (<1 m), and are selectively mined underground in Sri Lanka. Amorphous graphite is mined underground and usually extracted using selective room-and-pillar mining methods, similar to coal mining.

GRAPHITE BENEFICIATION

Graphite is naturally hydrophobic, and this property is conveniently leveraged via the use of flotation, targeting selective separation of hydrophobic graphite from hydrophilic gangue.

Comminution

Process flow-sheet development is predicated on specific deposit location, grade, and mineralogy. Generic flow sheets for processing hard rock and soft rock hosted ores are shown in Figures 1 and 2, respectively.

Hard Rock Hosted Graphite

Selection of the style of comminution circuit is predicated on ore competency and liberation size; selection of a dry or wet crushing circuit is heavily predicated on annual rainfall,

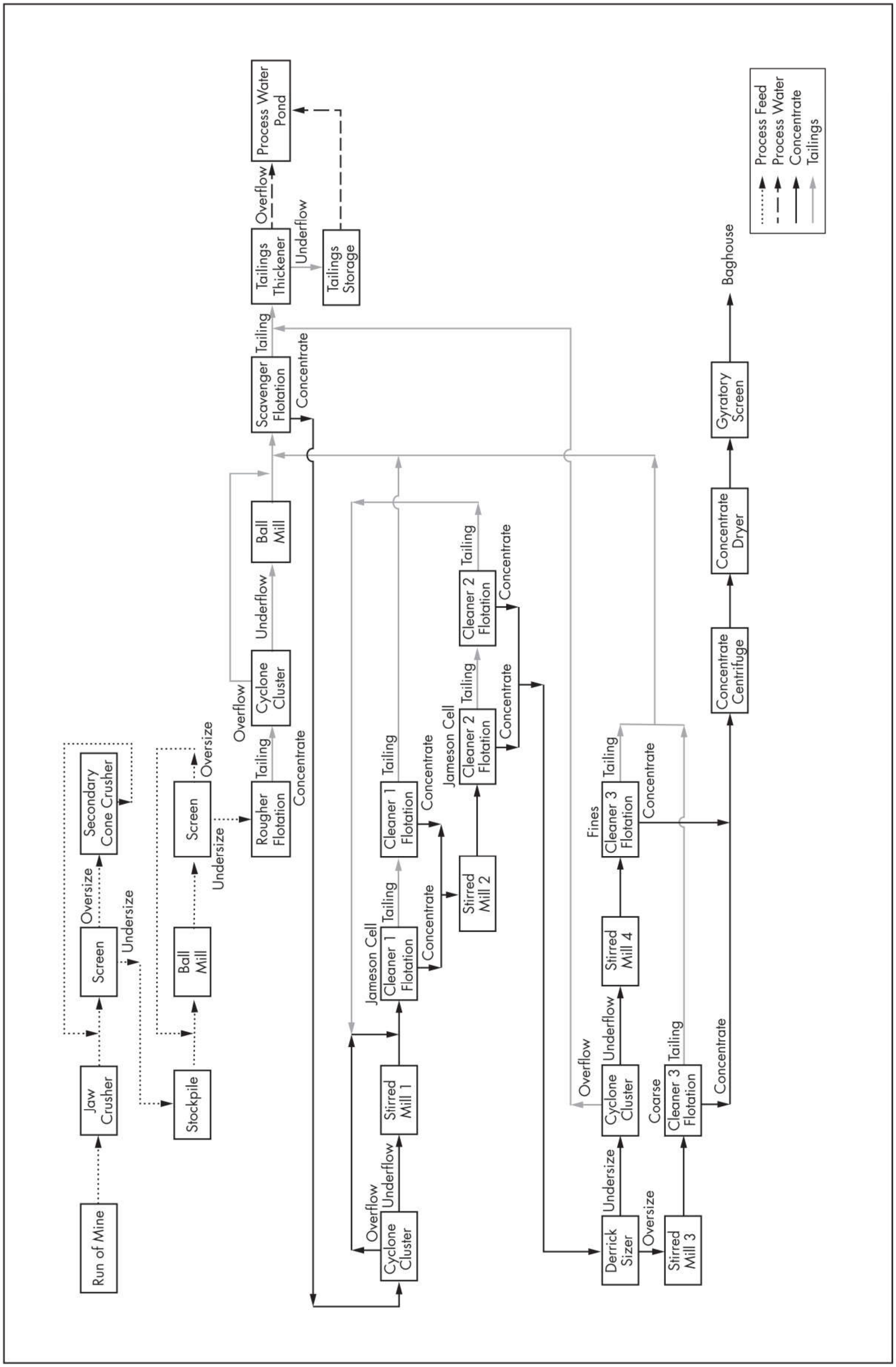


Figure 1 Competent host rock flow sheet

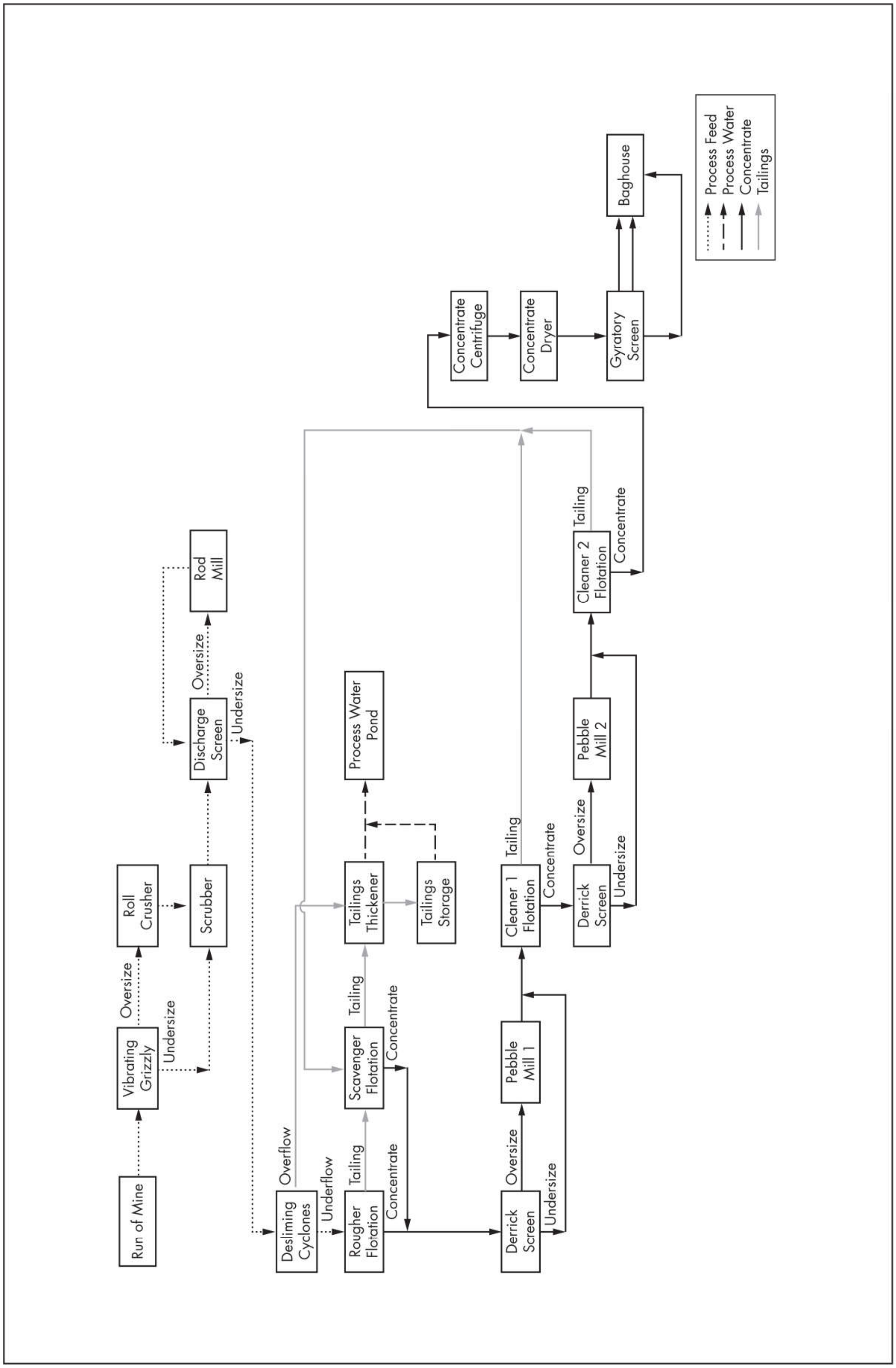


Figure 2 Soft host rock flow sheet

clay content, and location within the ore zone, either above or below the water table.

The hard rock example presented in Figure 1 incorporates the following unit processes:

- Secondary crushing based on primary jaw and closed-circuit secondary cone crushing
- Closed-circuit ball milling, targeting a moderately coarse grind (P_{80}) size, ranging from 250 to 500 µm

Tertiary crushing followed by closed-circuit rod mill grinding is a suitable alternative in cases where the graphite liberation size is coarser (nominally >700 µm). The inherent screening action characteristic of this style of milling provides a truncated mill discharge size distribution, minimizing generation of excess fines. The selection of rod milling, however, needs to be economically justifiable relative to semiautogenous grinding or coarse primary ball milling, the required throughput rate, and established ore competency.

Soft Rock Hosted Graphite

Graphite processing typical of that undertaken in western Madagascar in wet, soft, clay-rich saprolitic host is depicted in Figure 2 and includes the following:

- Coarse ROM screening using a vibrating grizzly. Grizzly oversize generally represents more competent fraction, and size reduction can usually be performed, maintaining control over top size via a coarse toothed roll crusher.
- Wet scrubbing utilizing a drum scrubber, accepting grizzly undersize and roll crushed oversize. Scrubber power requirements vary, depending on the power input, to ensure complete repulping of clay fraction. In selected cases, installation of a wave liner and the addition of a limited ball charge (2%–5%) can assist in breaking up coarse agglomerates.
- Scrubber discharge screened via a combination of coarse discharge trommel and vibrating screen. Oversize, nominally +1 mm reports for closed-circuit rod milling.
- Scrubber screen undersize, nominally –1 mm, is pumped to a hydrocyclone cluster operating at an approximate cut size of 45 µm for desliming and rejection of barren clay fraction and subgrade graphite.

Flotation

Graphite flotation is typically conducted based on initial roughing, targeting high graphite recovery. The adoption of a scavenger stage may be necessary, depending on the specific mineralogy, extent of liberation, and flotation kinetics. Rougher and scavenger concentrates are then subjected to a series of regrinding and selective cleaner flotation stages targeting high-grade concentrate >98% total carbon.

Reagents and Conditioning

Liberated graphite is naturally hydrophobic and can be floated readily using methyl isobutyl carbinol (MIBC) frother, diesel, or pine oil. A range of collectors are available that report improved gangue selectivity over more traditional reagents, also offering reduced reagent consumption based on blending with lower-cost diesel collector. Examples include proprietary reagents: IBM/D7, a hydrocarbon/turpen blend; and the Ekofol collector series, specifically Ekofol 452 G, Ekofol 452 GK, or Ekofol 452 GK 100.

Dispersants, such as sodium silicate or lactic acid, have been applied depending on gangue mineralogy and in specific cases where calcite entrainment is an issue. Lignin sulfonate can be used for dispersion.

Flotation can be conducted in the pH range 7–9 using soda ash as a pH modifier. Collector dosage depends on type; however, dosages ranging from 200 to 300 g/t flotation feed are typical. Lower primary collector dosages may be possible based on blending with lower-cost diesel. Graphite collectors tend to have some frothing properties; MIBC or proprietary reagent Senfroth are examples of typical graphite frothers.

Acceptable reagent conditioning can usually be achieved via moderate shear agitation ahead of rougher flotation based on 10-minute retention time; staged collector dosing can be applied to scavenger and selected cleaner stages as required.

Flotation Circuit Configuration

Flotation circuit configuration is ore specific; rougher flotation can be based on conventional, column, or flash flotation (depending on kinetics). Selected ores may also require the inclusion of a scavenger stage; however, in most cases, subsequent cleaning is performed based on a series of regrinding and cleaner stages.

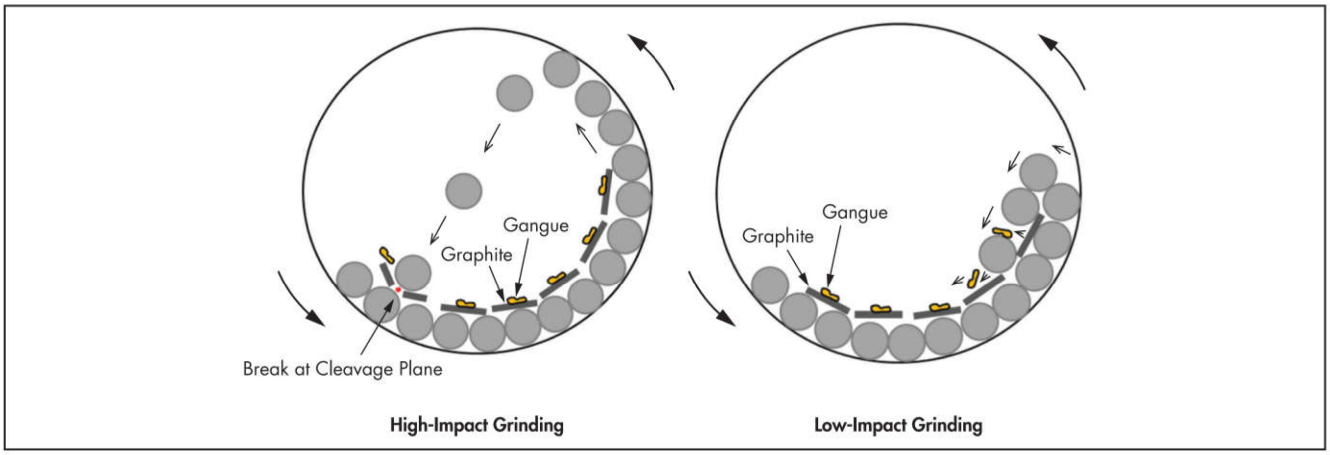
The hard rock hosted flow-sheet example presented in Figure 1 incorporates the following:

- Conventional rougher flotation is used in which rougher tailings report for hydrocyclone classification. Cyclone underflow (coarse fraction) is deferred for ball mill regrinding and combined regrind mill discharge. Cyclone overflow is subjected to final (conventional) scavenger stage flotation.
- Preferential stirred mill grinding of coarse fraction is maintained by reclassifying combined rougher and scavenger concentrate, deferring cyclone overflow (fines) through to stirred mill discharge.
- Two stages of whole concentrate cleaning are affected based on utilization of a combination of Jameson and conventional flotation cells to promote high selectivity in a cleaner and cleaner-scavenger configuration. Column cells can be used as an alternative to Jameson-style flotation cells.
- Improved grade recovery response over whole concentrate cleaning is leveraged by screening the first-stage cleaner concentrate using a stack sizer and undertaking split size cleaner flotation, again based on separate stirred mill regrinding and staged cleaning to produce final graphite concentrate.

Cleaner Stage Regrinding

Graphite concentrate regrinding, in most cases, differs relative to other commodities, given the layered structure of graphite, requirements to maintain flake size, as well as promote liberation from gangue. The grinding (or polishing) action required is better defined as shearing rather than pure impact grinding. This is illustrated in Figure 3. Graphite ores characterized by intercalated gangue exemplify the requirement to liberate the gangue based on shearing rather than impact breakage of graphite flake.

Dominant shearing breakage is affected via use of tower or stirred mill regrind stages utilizing ceramic media. Examples of pebble mill regrinding exist in the case of



Courtesy of IMO

Figure 3 Grinding action

soft rock applications, as depicted in Figure 2. In this case, selected producers operate pebble mills based on the following conditions:

- Variable speed, grate discharge, nominally operating as low as 35%–55% critical
- Pebble charge maintained at discharge trunnion liner, nominally representing 30%–35% volume
- Mill sized to promote graphite feed flow largely through pebble charge interstices
- Discharge grate comprising outer radial slots and upper radial blank liner plates to promote graphite interstitial flow with pulp lifters used as needed to increase volumetric capacity

Concentrate Recovery

Graphite flotation concentrates tend to retain relatively high moisture content and are required to be dried prior to final screening into separately sized flake products. Concentrate flake recovery is typically performed based on the following treatment:

- Thickening and transfer of thickened underflow to concentrate holding tankage
- Dewatering based on centrifuging or pressure filtration targeting 10%–15% cake moisture
- Concentrate drying, typically 400°–500°C
- Pneumatic or screw feeder transport to multideck concentrate sizing screens
- Graphite screening to form multiple (sized) products, final bagging, and off-site transport

Graphite drying can be performed using flash, twin screw, and rotary dryers. Fluid-bed dryers may be applicable; however, the selection of drying methodology should be supported by test work to ensure that agglomerates do not form ahead of final product screening. Electric and gas- or diesel-fired dryers are available, and selection of heat source is predicated on project location and surrounding infrastructure.

Dried product moisture may vary, depending on the achievable drier feed moisture and selected drying method. Product transport through to screening and bagging is typically pneumatic with best performance at ~0.1% moisture. Screw feeding can be utilized for higher moisture content.

Table 3 Graphite particle sizes for marketing

Sizing	Market Terminology
>300 μm (+48 mesh)	Extra-large or jumbo flake
>180 μm (–48 to +80 mesh)	Large flake
>150 μm (–80 to +100 mesh)	Medium flake
>75 μm (–100 to +200 mesh)	Small flake
<75 μm (–200 mesh)	Fine flake

Source: Triton Minerals 2017

Graphite product screening is performed using multideck screens. Gyratory screens can be used for this purpose to prepare separate flake products for bagging. Selection of screen cut size is predicted on the markets for the graphite products, as shown in Table 3.

Complementary Beneficiation Methods

Although flotation is the main process employed in graphite beneficiation flow sheets, gangue mineralization is specific to deposit location, geology, and location within the oxidation profile. Other selected unit processes are employed either to improve project economics via early gangue rejection or improve the flotation circuit grade recovery response. Examples include the following:

- **Screening.** In cases where barren or below-cutoff fraction exists at coarse size, simple dry screening can be used to affect early gangue rejection.
- **Magnetic beneficiation.** Selected graphite ores may be associated with iron-bearing gangue such as magnetite and pyrrhotite. Low- or medium-intensity drum magnetic separators have been used for rejection of liberated gangue.
- **Reverse flotation.** When graphite is associated with sulfide minerals, a separate stage of flotation with copper sulfate activator and xanthate collector(s) can be used to selectively float and reject sulfides, leaving upgraded graphite reporting to the reverse flotation tailings stream.

MARKET AND PRODUCT APPLICATIONS

Graphite production has undergone a resurgence in recent times as a function of growth and demand for high-grade graphite concentrate input to lithium ion battery and fuel cell manufacture.

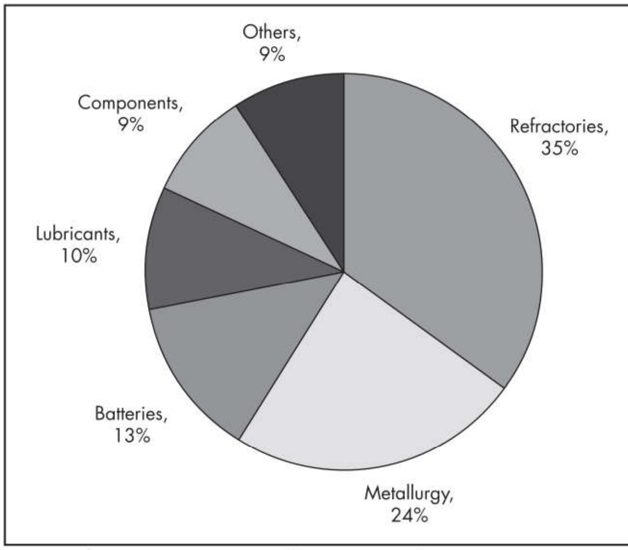
Product applications for graphite concentrates are wide ranging. Volume distribution across traditional and growth markets is summarized in Figure 4 (the proportions are estimated), and typical grade and size specifications are presented in Table 4.

Marketing and Downstream Processing

The Harmonized Tariff Codes for natural graphite are 250410 (natural, in powder or in flakes) and 250490 (natural, in other forms, excluding powder or flakes) and 380110 (artificial graphite). Natural and synthetic graphite is shipped internationally in either paper bags or 1-t bulk bags and locally may also be shipped in bulk road tankers.

Downstream production is carried out by specialist processors such as Asbury Carbons, Superior Graphite, and GrafTech International in the United States. For example, Asbury processes, upgrades, and trades many types of carbons, including natural and synthetic graphite, coke, and coal, and sells to a wide range of end markets including lubricants, refractories, and foundry industries.

Superior Graphite specializes in electrothermal purification technologies, engineered graphite electrodes, advanced ceramic shapes and powders, precision particle processing, and carbon coatings. GrafTech International focuses on synthetic graphite products and markets, particularly electrodes, but the company also manufactures products based on natural graphite for thermal applications in the electronics industry and for sealants. The company buys flake graphite from sources around the world to manufacture into expandable graphite.



Source: Olson 2017; Scogings et al. 2015a, 2015b

Figure 4 Estimated graphite market and product applications

Table 4 Typical graphite concentrate market specifications

Application	Total Graphitic Carbon, % Lower	Total Graphitic Carbon, % Upper	Size, μm Lower	Size, μm Upper
Steel and Refractory Additives				
Refractories	85.0	90.00	150	710
Crucibles	85.0	90.00	75	150
Expanded graphite	90.0	98.00	200	1,700
Foundry additives	40.0	70.00	53	75
Core and mold washes	70.0	90.00	1	75
Recarburizing steel	98.0	99.00	1	5
Lubricants Automotive and Electrical				
Lubricants and releasing agents	95.0	99.00	25	300
Brake and clutch linings	95.0	98.00	1	75
Bearings	90.0	93.00	150	500
Gaskets	80.0	99.90	40	300
Carbon brushes	95.0	99.00	1	53
Electrical	93.0	95.00	150	500
Batteries and Fuel Cells				
Dry cell batteries	88.0	90.00	1	106
Alkaline batteries	90.0	99.90	5	75
Lead acid batteries	90.0	95.00	5	58
Lithium ion batteries	99.0	99.90	25	48
Spherical graphite	99.9	99.99	1	48
Fuel cells	99.9	99.99	40	150
Specialty Products				
Powder metallurgy	95.0	99.00	10	50
Polymer additives	50.0	85.00	5	15
Conductive polymers and plastics	99.0	99.99	3	38
Graphite powders	85.0	99.99	3	38

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