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Review Article

A Mini Review on Flotation Techniques and Reagents Used in Graphite Beneficiation

N. Vasumathi,[1,2] **Anshuli Sarjekar**,[3] **Hrishikesh Chandrayan**,[3] **K. Chennakesavulu**,[4] **G. Ramanjaneya Reddy**,[4] **T. V. Vijaya Kumar**,[1] **Nour Sh. El-Gendy**,[5,6] **and S. J. Gopalkrishna**[2]

[1]*CSIR National Metallurgical Laboratory Madras Centre, CSIR Madras Complex Taramani, Chennai 600113, India*
[2]*Vijayanagar Sri Krishnadevaraya University Post-Graduate Centre, Nandihalli, Ballari 583119, India*
[3]*Birla Institute of Technology and Science, Pilani, India*
[4]*Department of Chemistry and Centre for Nanoscience and Nanotechnology, International Research Centre, Sathyabama Institute of Science and Technology (Deemed to be University), Chennai 600119, India*
[5]*Egyptian Petroleum Research Institute (EPRI), Nasr City, P.O. 11727, Cairo, Egypt*
[6]*Center of Excellence, October University for Modern Sciences and Arts (MSA), 6th of October City, P.O. 12566, Giza, Egypt*

Correspondence should be addressed to N. Vasumathi; vasumatisamy@gmail.com and Nour Sh. El-Gendy; nourepri@yahoo.com

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Due to its numerous and major industrial uses, graphite is one of the significant carbon allotropes. Refractories and batteries are only a couple of the many uses for graphite. A growing market wants high-purity graphite with big flakes. Since there are fewer naturally occurring high-grade graphite ores, low-grade ores must be processed to increase their value to meet the rising demand, which is predicted to increase by >700% by 2025 due to the adoption of electric vehicles. Since graphite is inherently hydrophobic, flotation is frequently used to beneficiate low-grade ores. The pretreatment process, both conventional and unconventional; liberation/grinding methods; flotation methods like mechanical froth flotation, column flotation, ultrasound-assisted flotation, and electroflotation; and more emphasis on various flotation reagents are all covered in this review of beneficiation techniques. This review also focuses on the different types of flotation reagents that are used to separate graphite, such as conventional reagents and possible nonconventional environmentally friendly reagents.

1. Introduction

Graphite is a natural crystalline allotrope of carbon that is greenish-black and shiny [1]. K. W. Scheele first chemically characterised graphite in 1779, and A. G. Werner later gave it the term "graphite," which was derived from the Greek word "grapho," which means "I write" [2]. There are many different physical and structural forms of carbon that exist in nature [3]. Van der Waals forces cause the parallel sheets that make up graphite's structure to be weakly attracted to one another [3]. Carbon nanotubes, diamonds, and fullerenes are also crystalline materials [4]. Carbon atoms in graphite are sp^2 hybrids with "*pi*" electrons in plane P-orbitals [5–8]. One out-of-plane electron per carbon atom gives carbon its metal-like characteristics, such as lustre and high electrical and thermal conductivities [9]. Being an allotrope of carbon, it also possesses nonmetallic qualities, including inertness and high lubricity. It is the perfect material for use in fuel cells, refractories, lithium-ion batteries, fibre optics, and electrical vehicles because it combines metallic and nonmetallic qualities [4]. Graphite can take on a variety of shapes, including hexagonal, rhombohedral, and turbostratic structures [6, 7]. According to Jin et al. [10], there are three different forms of naturally occurring graphite: crystalline (flake), microcrystalline (amorphous), and vein (lump) [10]. Their attributes are presented in Table 1. Metamorphism of carbon compounds in sedimentary rocks produces graphite. The majority of it is

Table 1: Properties of different graphite forms [4, 6, 11, 12].

Property	Amorphous	Flake	Lump
Occurrence	Formed as a result of anthracite coal seams metamorphosing	The development of small flakes inside the rock is the result of regional metamorphism	Lump graphite is created when hydrothermal activity changes the carbon compounds inside the rock
Description	Most prevalent, carbon quality: 20%–40% (low)	Good abundance, carbon grade <90%	Carbon grade >90%, rarest in supply
Major producers	China, North Korea, Mexico, and Austria	China, India, Madagascar, Mexico, and Brazil	Sri Lanka
International market value	Low	Good	Very high
Market price/ton	300–500 USD	500–3,000 USD	3,000–6,000 USD
Morphology	Fine granular structure	Flaky, flat, plate-like particles	Massive fibrous aggregates

Table 2: Specifications and uses of graphite [14].

End products	Percentage of graphite used	The quality of the graphite used	
		Fixed carbon (F.C.) (%)	Size (micron)
Mag-carb refractories	12	87–90	150–710
Alumina-carb (graphitised) alumina refractories	8–10	85 min	150–500
Clay-bonded crucibles	60–65	~80	149–841
Expanded (or flexible) graphite foils and products-based thereon (e.g., sealing gaskets in refineries, fuel pumps, and automobiles)	100	90 min. (Preferably + 99)	250–1800
Pencil	50–60	+95–98	50 max
Brake-linings	1–15	98 nub,	75 max
Foundry	—	40–70	53–75
Batteries			
(a) Dry cells	—	88 min	75 max
(b) Alkaline	—	98 min	5–75
Brushes	—	Usually 99	Usually less than 53
Lubricants	—	98–99	53–106
Sintered products (e.g., clog wheels)	—	98-99	5
Paint	Up to 75	50–55 75% nub	Amorphous powder flake
Braid used for sealing (e.g., on a ship)	40–50	95 min	—
Graphitized grease (used in seamless steel tube manufacturing)	—	+99	38 max
Colloidal graphite	100	99.9	Colloidal

found in the rocks' fractures, pockets, veins, and scattered forms [2, 13]. The most sought-after of these kinds, flake, is found inside the rock in flaky form. The viability of mining a graphite ore depends on how many flakes are there. Due to its superior heat and erosion resistance compared to other graphite forms, refractory manufacturers are the largest consumers of flaked graphite. In addition, the flake form of graphite is preferred since lump graphite is more expensive and less common. The most common type of graphite, amorphous graphite, has significant commercial value and is one of the top stocks. With the right processing, one can achieve up to 99% purity from this low-grade ore [10]. Lump graphite has a high market value since it is very rare and has higher purity and crystallinity than amorphous graphite. This limited its use to applications that required its exceptional qualities, including high electrical conductivity and purity.

By accident, Edward G. Acheson created synthetic graphite by heating carborundum (SiC) at a high temperature, which produced extremely pure graphite [12]. Graphite can currently be produced in a variety of ways, depending on the purity required.

More than 800 million tonnes of viable graphite are thought to be in global reserves. However, the estimated global graphite reserves are only 300 million tonnes. Turkey (30%), Brazil (24%), China (24.34%), Mozambique (5.67%), Tanzania (5.67%), and India (2.67%) make up the world's graphite reserves [14]. Other significant countries that produce graphite are Sri Lanka, Canada, Europe, Mexico, and the United States [4]. In 2017, 1.03 million tonnes of graphite were produced, with 88% of that production coming from China, 8% from Brazil, and 3% from India, according to the US Geological Survey. The top nations looking into new natural supply sources are Canada and Brazil [6, 14].

Natural graphite is used in lubricants, brake linings, batteries, steel production, foundries, and refractories [3, 8, 15]. In addition to its particle size, the proportion of fixed carbon in graphite is extremely important for a variety of graphite uses (Table 2). While synthetic graphite is utilized as a neutron moderator, radar adsorbent materials, electrodes, graphite powder, and other things [3, 16], there are numerous ongoing research projects to investigate novel uses for graphite. A few of them include preventing fires, cleaning up oil spills, and removing arsenic from water, among others [17]. It is clear from Table 2 that the majority of businesses use natural graphite demand purity levels of at least 90%. Since lump graphite with a purity of >90% is uncommonly abundant, beneficiating lower-quality graphite to the desired grade (typically >90%) becomes imperative. Due to the presence of mineral acids in them, current conventional procedures like acid leaching are detrimental to the environment [4]. Hydrochloric acid is the only mineral acid that is safe, but it is ineffective for acid leaching [4, 18]. Due to innovative uses for the material and possible high future output, there will be an increase in the beneficiation of low-quality graphite ore reserves around the world. Therefore, methods of beneficiation that does not hurt the environment will be very important for the graphite industry to grow.

2. Microwave Pretreatment

It is necessary to separate or break down the impurities that are present in the ores. Microwave irradiation, first proposed by Walkiewicz in 1991, is a great, environmentally friendly way to heat the ore. That process results in isolated fractures at the intergranular and transgranular regions without triggering catastrophic failure, which results in cracks along the grain boundaries. This breaks down the impurities that are stuck in a "honeycomb" pattern [19]. According to Özbayoğlu et al. [20], the eliminated contaminants are primarily moisture, sulphur, and other volatile salts. For a low-grade graphite sample, effective impurity removal results in a marked rise in the fixed carbon content in the concentrates. That technique has important advantages like lowering the work index and reducing the wear and tear on the mill, mill liners, and grinding media [19, 21–23]. It has been discovered that such a method is now quite effective for the flotation of coal and ilmenite ores, so it can be expected that it has good potential for beneficiating graphite as well [24, 25].

3. Grinding

3.1. Conventional Grinding Methods: Ball and Rod Milling. The two most used methods for grinding graphite ore are ball and rod mills:

A cylindrical shell that spins about its axis is used in ball milling. Graphite ore and chrome steel or stainless steel balls are placed inside the shell. An abrasion-resistant material, usually a manganese-steel alloy, is used to make the interior of the object. Grinding is mostly accomplished through the impact of the balls on the edges of the ore particle pile at the bottom. Secondarily, the ore is ground by the friction created by the slipping balls [26]. This results in size reduction by means of compression and shearing forces, which arrange the ore particles in an anisotropic manner [6, 27]. High-intensity milling, on the other hand, results in amorphous carbon, compromising flake size [28, 29]. Ball mills are easy to use and cheap to run [6, 30].

A rod mill has a cylindrical body similar to a ball mill, except instead of balls, it uses rods. The rod system consumes 35–40% of the mill's capacity [31]. Large particles are crushed to a smaller average particle size in a rod mill by being trapped between the rods and moving toward the discharge end of the rod. As a result, the size of the particles at the two ends of the rods varies and is dependent on the mill's length, feed rate, and grinding speed [32]. A crucial aspect of this approach is its improved ability to grind big particles. Rod mills are chosen over other types of grinding whenever the ore is sticky. Compared to ball milling, rod milling generally does less harm to the size and shape of the flake. Due to the relatively smaller surface area of the rods, the rod mill uses more energy [31].

3.2. Nonconventional Grinding and Regrinding: Stirred Milling, Jet Milling, Delamination, and Attrition Milling. Traditional grinding methods like ball milling or rod milling do not take into account impurities that exist in the layered graphite [6]. In contrast to strong intralayer covalent bonding, the weak Van der Waals forces between the graphite layers are easily overcome [3, 33]. Such layered minerals produce an anisotropic structure upon grinding. Thus, abrasive forces must be applied instead of compressive or shearing forces [34] that can be achieved using a stirred mill, which consists of a cylindrical shell, stirrer, shear blade, and distribution disc. The stirred mill rotates the pulp while agitating the ore to grind it while minimizing impact force and preventing overgrinding. It was reported that stirred milling causes less damage to flake shape and size as compared to rod milling and ball milling because the grinding media or pulp rubs against each other due to various rotational speeds, resulting in an active force leading to the release of layers of the mineral [33]. Jet milling, on the other hand, uses high-impact stress to keep the ore's flaky structure and nonuniform shape on large particles [35].

Earlier, it was believed that graphite regrinding, which limited the maximum fixed carbon concentration to 95%, was useless because graphite coats gangue particles and makes them floatable [36]. The graphite middling delaminates when it is reground in a slow-speed ball mill employing a flint pebble grinding media. This method is superior to traditional milling for the preparation of flake graphite since it has little effect on the size and form of the graphite flakes. This method produced fixed carbon contents of up to 98% [37].

Attrition milling can be utilized as the final stage of liberation by grinding. The attrition method is used to selectively separate tiny particles. This is a very effective method if a small particle size of graphite is required for its usage as a lubricant. Attrition can keep the flaky form and crystallinity of graphite while reducing 90% of a 150 μm sample to 1 μm [38].

4. Gravity Separation

This technique is based on the fundamental idea of the disparity between the specific gravities of the ore and contaminants. The simplicity of the process, cost-effectiveness, and environmental friendliness are this method's defining characteristics [39]. It has been reported that when fine graphite particles (less than 150 μm) are passed through a hydraulic classifier, they consume 34% less acid in the leaching process.

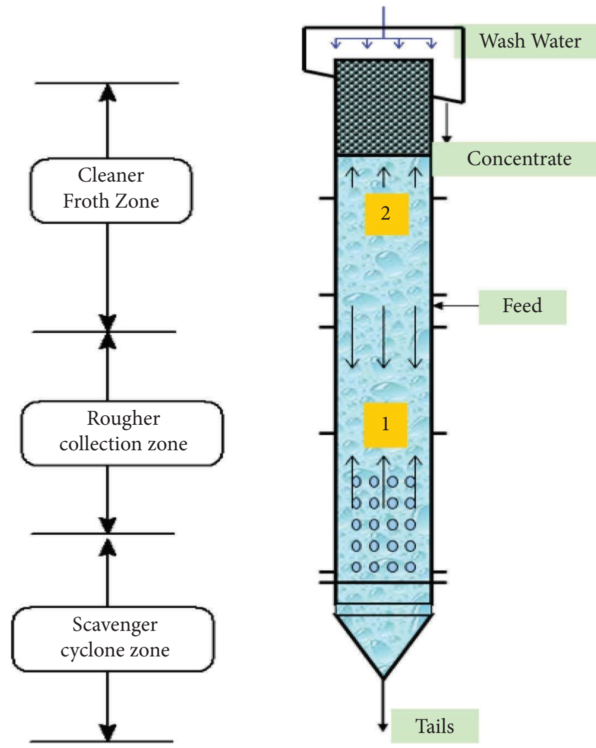

Figure 1: Schematic diagram of flotation column.

Due to the technique's increased environmental friendliness, it is thought to be even more environmentally beneficial than traditional froth flotation [40, 41]. Gravity separation can also be used if it is necessary to concentrate a specific component from the tailings [6].

5. Froth Flotation

The separation of hydrophobic minerals from hydrophilic contaminants is an important application of this technique. It is a physiochemical technique that August and Adolph carried out for graphite for the first time in 1877 [40, 42]. This concentrates them by taking advantage of the hydrophobic properties of graphite and related ores. The studies indicated that when compared to other concentration processes, the froth flotation process required three to four times fewer samples to produce the same amount of concentrated ore. When compared to alternative techniques, it can also dramatically lower the expense of tailing management and treatment [43]. Depending on the application, two alternative types of flotation methods are used for graphite on an industrial scale: mechanical and column flotation.

5.1. Column Flotation. This occurs in a cylindrical flotation column. With the aid of a bubble generator, gas bubbles are introduced from the bottom of the column while the slurry is fed from the top. Gas particles disperse into the slurry as a result of a concentration differential. A counter-current

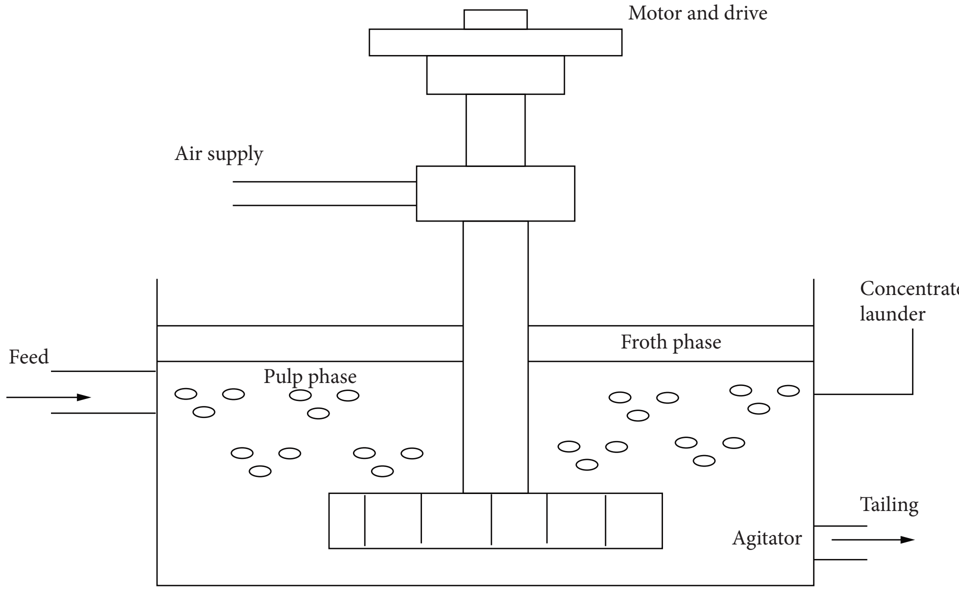

Figure 2: A representation of flotation cell.

laminar flow results from this. As a result of this action, there is a high relative velocity and an increased likelihood of a collision [44]. The froth zone, collection zone, and scavenger cyclone zone are the three zones that form in the flotation column, as shown in Figure 1. When water (a diluent) is added, froth with hydrophobic pure graphite particles forms at the top of the column [45]. The froth selectivity increases with the froth height. The improved ore and wash water mixing caused by the closer proximity of the wash water inlet to the pulp-froth interface is what accounts for the increased selectivity [46]. The froth zone has an air holdup (volume of liquid displaced by air) of about 80% [44].

Superficial gas velocity is one of the most significant variables in the column flotation process. Low gas holdup due to a lower gas velocity of the flow shows a negative impact on the grade and recovery of the ore. The reduced turbulence caused by column flotation, in addition to its low operating cost, is a significant benefit. The energy that the turbulence contributes leads to the unwanted dissociation of the mineral particle from the bubble. Negative bias is used to keep the flow of tailings lower than the feed flow to recover more flaky graphite [44, 47, 48]. The bubbles in column flotation have a large lower limit in terms of diameter. As a result, microparticles find it challenging to collide with the froth. The water's streamlines allow the fine particles to move. The float recovery is decreased in this way, but only for fine and ultrafine particles [48, 49].

5.2. Flotation by Mechanical Cell. This process is used to beneficiate mineral particles that are difficult to remove. These are the tiny particles of graphite. Figure 2 shows an example of flotation cell, as reported by Kuan [50]. In mechanical flotation cells, froth is produced by agitation with a rotating impeller. The high-speed impellers release air bubbles into the system [5]. The impeller rotation speed is a crucial process parameter. Studies show that controlling bubble-particle adhesion depends on this component [51]. The relative velocity of bubble and particles close to the impeller only matters in this sort of cell. As a result, there are fewer collisions.

In addition, the residence period is shorter than the overall amount of time a bubble spends in the pulp. For these reasons, less concentration of graphite particles is caused. pH, promoter addition, feed size, impeller speed, viscosity, and collector dose are the major factors [44, 52, 53]. The lack of spargers in mechanical cells gives them a significant advantage over flotation columns. In flotation columns, spargers are employed to create bubbles. They need constant upkeep because they are vulnerable to particle obstruction, degradation, and frequent malfunctions. Another benefit of mechanical cells is their ease of use and lower cost for small-scale applications [54].

5.3. Reagents Used in Graphite Flotation. To create a pulp environment that is favourable for separating undesirable gangue particles from valuable minerals, flotation reagents are used [55]. The qualities of the reagents, such as collectors, frothers, and depressants, which are crucial to the effectiveness of the flotation process of concentration, include mineral hydrophobicity, bubble size, contact angle, bubble formation, and particle adherence. These properties are discussed below in detail.

5.3.1. Frother. Nonionic heteropolar compounds known as "frothers" can stabilise froth and selectively restrict the entrainment of gangue particles into it. They promote greater bubble formation when disseminated. While the hydrophobic end of the frother selectively adsorbs on air, the polar end forms a hydrogen bond with water. This reduces the water's surface tension and improves foam stability [5]. Figure 3 shows a schematic diagram for the interaction of

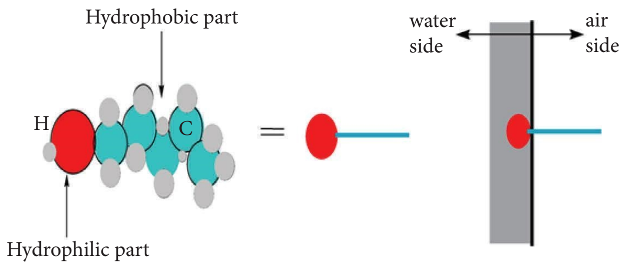

Figure 3: Interaction of frother with graphite and hydrophilic and hydrophobic parts.

frother with graphite and the hydrophilic and hydrophobic parts [5]. Only frother-acting surfactants are used when there is no oxidation in the graphite ore in any shape or form. Alcohols, alkoxy paraffin, polyglycols, and polyglycol ethers are some of the frothers that are easy to buy [56].

When frothers are added, graphite that has little to no contamination floats with ease. Methyl isobutyl carbinol (MIBC) and fuel oil are frequently used frothers [37]. Isoctanol, pine oil, MIBC, and tri (propylene glycol) butyl ether were the four frothers that were compared to each other to provide better recovery and grade on graphite flotation. The fixed carbon content of the recovered graphite is seen to decrease as the frother dosage is increased. According to Öney and Samanli [57], MIBC was the best of the four blenders.

For example, pine oil and Dowfroth are better alternatives to MIBC because they are safer for the environment [58]. A popular frother is made of pine oil, which is obtained from pine stumps or turpentine [4]. However, due to its irritating properties, which are indicated in Table 3, the use of pine oil is gradually decreasing and frequently prohibited. In addition, when employed as a frother, coal oil is more discerning than fuel oil [2].

For graphite flotation, the MIBC, pine oil, cresylic acid, TEB, and Dowfroth 200 frothers were examined and compared [56]. These are compared for risk-rated attributes such as flash point, exposure, and environmental risks, as seen in Table 3. According to the information given in Table 3, Dowfroth 200 is one of the safest frothers.

A numeric term called "hydrophilic-lipophilic balance" (HLB) comes into play as the frothing ability of a frother is considered. This indicates the ratio of hydrophilic to lipophilic groups present in the frother. Dowfroth 400, Nasfroth AHE, Dowfroth 200, Nasfroth 301, and MIBC were evaluated as frothers for graphite with HLB values of 9.9, 8.2, 8, 6.5, and 6.1, respectively. The flotation performance increases in the order of Nasfroth AHE < MIBC < Dowfroth 400 < Dowfroth 200 < Nasfroth 301. Low HLB and low molecular weight of the frother increase the flotation yield [59].

The polar interactions that result from the wettability of hydrophobic solids (like graphite) with polar adsorbates are detrimental to the flotation process because they reduce the adherence of the mineral to the air bubbles. It is important to develop a technique that takes into account the polar interactions between substances that have previously been adsorbed and those in solution. Jańczuk et al. [59] list as variables the type of frother, the concentration, the surface tension of the solvent, and the contact angle.

5.3.2. Collector. The compounds that have a polar and a nonpolar group joined together are called collectors. The primary purpose of the collector is to make the mineral's surface hydrophobic to improve the mineral's capacity to float [37, 55]. Since graphite is a hydrophobic mineral, it should float on the water's surface by nature [60]. But contamination of the graphite surface in an oxidising environment, whether from simple oxidation, nitration, or the presence of other hydrophilic impurities, causes the deposition of excess charges on the surface, similar to those of a hydrophilic solid, and this calls for the addition of a collector, as shown in Figure 4. The hydrophobic layer of the nonpolar surfactant that serves as the collector is applied to this polluted hydrophilic surface [56]. In the flotation of graphite, hydrocarbons such as paraffin, diesel, and kerosene are used, as well as ionic collectors such as potassium amyl (or ethyl) xanthates, dithiocarbamates, and dithiophosphate [57, 61, 62]. Typically, hydrophobic materials like graphite are floated using nonpolar collectors such as kerosene, diesel, and fuel oil [53, 55, 61, 63, 64]. When the collector properties of diesel, n-dodecane, and kerosene oil were compared, diesel produced the best outcomes. The performance of dodecane and kerosene is dose dependent. Kerosene was discovered to be more efficient at low collector dosages [57]. In aqueous media, diesel and kerosene are less soluble, and their emulsification improves flotation performance. Hexanol and octanol were used as coemulsifiers in this experiment. Diesel-hexanol systems are more efficient than diesel-octanol systems because diesel is more evenly dispersed in hexanol than in octanol, which leads to smaller collector droplet sizes and more collisions between mineral particles and the coemulsified collector, improving recovery [65]. In contrast to the diesel-pine oil system, which only fixed 90% of the carbon, the IBM/07 mixture of different hydrocarbons and terpenes was used as a collector to fix 96% of the carbon [66].

According to the safety data sheet (SDS), the Greenness Index, an evaluation tool, assesses the reagents based on the parameters of health impact, general properties, odor, fire safety, and stability. It offers useful guidance for making the most sustainable reagent choice [67]. Most commercially available surfactants are made with chemicals because they are toxic, do not break down, and may make harmful byproducts [68].

It has been discovered that using a single reagent, such as the alcohol-ether-based collector "Sokem 705C," is more environmentally friendly, more effective, and more economical than using a dual reagent system like a diesel-pine oil system [64]. The carbohydrate-attached lipids known as glycolipids, which are generated from amino acids, carbohydrates, and vegetable oils, have the potential to replace nonrenewable petroleum-based goods like diesel and kerosene. As is done by a group of researchers, where they have

TABLE 3: Safety risk ratings on flotation frothers [58].

Reagents	Flash point °C	Risk rating	Exposure risk	Risk rating	Environmental risk	Risk rating	Total risk rating
Aliphatic alcohol							
MIBC	39	5	Odour irritant	3	Minimal	2	10
Cyclic alcohols							
Pine oil $C_{10}H_{18}O$	78	3	Irritant	2	Minimal	2	7
Aromatic alcohols							
Cresylic acid $CH_3C_6H_4OH$	81	3	Irritant	2	Harmful	4	9
Alkoxy-type							
1,1,3-Triethoxy butane $C_{10}H_{22}O_3$	80	3	Irritant	2	Nonhazardous	2	7
Polyglycol-type							
Dowfroth 200	195	1	Minimal	1	Minimal	2	4

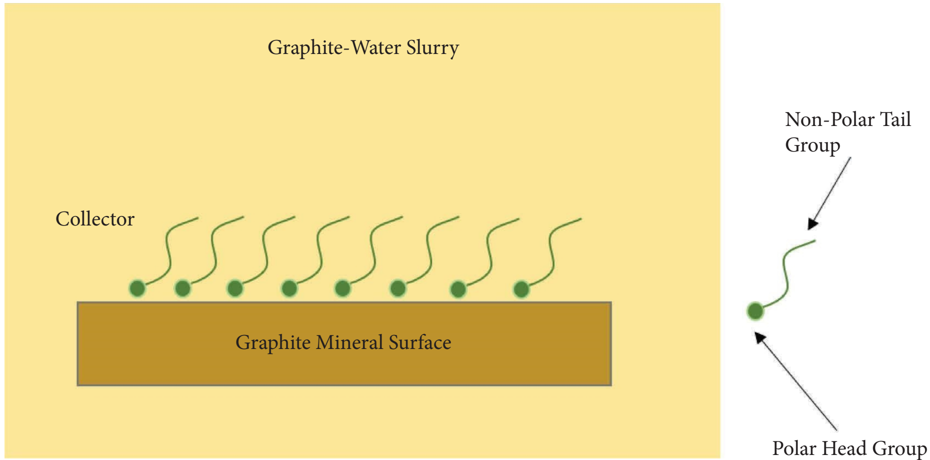

Figure 4: Polar ends of collector interaction on the surface of graphite ore particle.

replaced oleic acid with soyabean oil as collector and have achieved comparable results [69]. In addition, biosurfactants are molecules with a polar and a nonpolar group linked to them that are biologically manufactured by microorganisms and are capable of creating outcomes similar to those of synthetic surfactants [68].

A secondary source of graphite is the depleted Li-ion battery. Lithium carbonate and graphite, which are extracted via a unique method termed "grinding flotation," are the two valuables that result after purification. As a flotation collector, decane, dodecane, and Fenton reagent (a combination of ferrous sulphate and hydrogen peroxide) can be employed [9, 70]. If this lithium is made chemically from lithium carbonate, it can also help the economy in other ways.

When microflotation of amorphous graphite was carried out with different drop sizes of the collector, it was observed that the rate constant of the reaction and the recovery increased with a decrement in the droplet size. This behaviour is explained by the principle that the smaller the droplet size of the collector, the more the surface area is available to be exposed to the hydrophobic part. Thus, the collision of graphite particles with the bubbles becomes faster and more numerous, also the bubble strength is found to increase [4, 71, 72]. With a smaller droplet size, and the reduced contact surface area, resulting in less consumption of the collector, hence saving reagent costs.

5.3.3. Depressant. The chemical compounds known as depressants, often referred to as inhibitors, specifically block the flotation of other minerals while not affecting the flotation of the desired mineral. In general, there are two types of depressants: organic and inorganic [17]. Graphite is depressed using inorganic substances such as sodium silicate, sodium cyanide, lime, and sodium sulphite [53, 55, 64]. These use electrostatic interactions to keep the foam stable [73]. In contrast to sodium cyanide, which is used to depress pyrite, sodium silicate is utilized to depress siliceous gangue particles. Dextrin, starch, tannic acid, and carboxymethyl cellulose are examples of organic salts that also possess depressant-like characteristics [6, 55, 73–75]. When used with hydrophobic minerals like graphite, they perform incredibly well. They use steric effects to stabilise the pulp suspension [73].

6. Electroflotation

Due to the inability of current conventional flotation methods to recover a considerable number of tiny and ultrafine graphite particles due to poor bubble-particle collision efficiency, the problem of reduced recovery is observed in low-grade graphite ores [49, 76]. This lowers the process's net profitability in large-scale operations. Microbubbles are produced by the electroflotation process during the electrolysis of water, during which hydrogen and oxygen are released at cathodic and anodic surfaces, respectively [49, 77, 78]. Greater "apparent particle size" is the outcome of flocculation, which is triggered by smaller bubbles [49, 79, 80]. This speeds up the process of bubble-particle adhesion. Due to the formation of hydrogen and oxygen bubbles, that is more active for hydrophobic materials than air bubbles created by conventional approaches. This method claims a higher efficiency, with a more control over the bubble flow. Consequently, the electroflotation can be a very successful method for the flotation of ultra-fine graphite.

7. Ultrasound-Assisted Flotation

High-purity flake graphite has a high economic value in the markets. Because the trapped impurities are transported with the graphite in the froth during the traditional flotation process, getting high-purity flake graphite is quite challenging [81–83]. The maximum purity of graphite that can be produced using conventional flotation is 95%, while this also depends on parameters including the ore's grade, number of flotation stages, and percentage crystallinity [4]. The three stages of ultrasound treatment—rougher stage, cleaner stage, and recleaner stage—are based on a difference in the strengths of "attachment of locked impurities" and "graphite flake structure." In contrast to the traditional

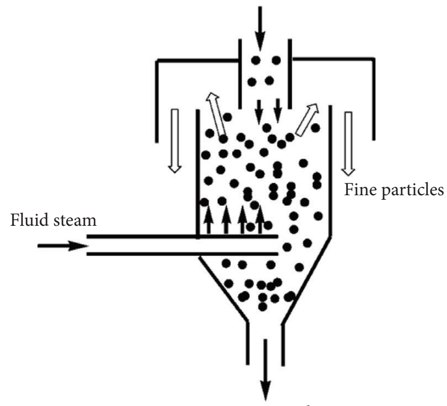

FIGURE 5: Air elutriation mechanism of coarse particles.

grinding method, it selectively removes the trapped impurities while causing relatively little harm to the flake size and shape. Consequently, it promises to be a promising industrial tool [84].

8. Air Elutriation

Compared to amorphous graphite, flake graphite has a much higher market value (Table 1). However, the graphite produced by the froth flotation method is a blend of flake and amorphous graphite. Amorphous graphite should be separated from flake graphite for the greatest economic potential. For the same, air elutriation is employed. Figure 5 shows the air elutriation mechanism of coarse particles [85]. In the large-scale configuration, blowers are used to create an upward air flow at the base of vertical pipes. At almost one-third of the length of the entire pipe from the bottom, mixed graphite feed is added. The air flow velocity is restricted to between 0.9 and 4.6 m/s. The amorphous graphite with any remaining impurities falls to the bottom of the pipe, while pure graphite flake rises to the top [6, 86].

9. Flushing Process

For high-quality requirements, the amorphous graphite obtained from the bottom product of air elutriation can be further cleaned with other adhering contaminants by a flushing procedure. The graphite particles are put through a kerosene-based oil phase in this process before being transferred to an aqueous suspension utilizing sodium carbonate as a surfactant. High-speed centrifugation removes the fine clay and ash contaminants by generating little oil droplets [6, 87].

10. Techno Economics

Cost and energy requirements of beneficiation by flotation:

For the flotation of graphite ore, two main costs are involved: the cost of ore material and the cost incurred in the beneficiation process. The costs involved in the beneficiation process includes plant maintenance, consumables, electricity supplies, utilities cost, cost of flotation reagents (collector, frother, and depressant), and cost of skilled and unskilled labourers.

For the beneficiation process of the graphite ore as per the prefeasibility report of Bainibasa Graphite Mining and Beneficiation Project, Orissa, the feed throughput of crude graphite ore is 13,272 TPA which will be processed to obtain 841 TPA of desirable clean graphite with 85% and 65% FC content of the purified graphite. The total water requirement is 130 kilolitre/day. The cost per tonne for the ore material is between 11,141 and 14,766 INR/ton of the finished product for the first five years of the flotation plant installation. While the costs involved in the beneficiation process per ton is between 10,467 and 11,266 INR/ton of the finished product for the first five years after the plant installation, so that the total amount spent on processing the crude ore to the desired purified ore is between 21,608 and 26,032 INR/ton of the finished product.

10.1. Energy Requirement. The operational capacity of beneficiation is 30 TPH. The hours of plant operation thus are 13,272 TPA/30 TPH = 442.4 hrs/annum ~443 hrs/annum. The power supply is of 400 kVA = 400 kW = 400 kJ/sec.

The energy requirements of the beneficiation plant alone are = (power of the supply) × (hours of operation of beneficiation plant) = 400 kJ/sec × 443 hrs × 60 min/hr × 60 min/sec = 637,920,000 kJ = 6,37,920 MJ.

11. Comparative Assessment of Various Beneficiation Techniques

Merits and demerits of different beneficiation techniques are summarized in Table 4.

Comminution is only responsible for reducing the particle size and hence resulting in different particle-size distribution. The benefits are that we can bring the ore particles in the industrial demand range and enhance the surface area for the improved impact of downstream processes. This method to very less extent can eliminate the gangue particles. Further processing is recommended to meet the high-end purity standards for industrial uses. Microwave irradiation facilitates easy and selective heating, is more energy efficient, and makes the output feed environmentally less benign as it releases sulphurous and nitrous products in the gaseous form. But it releases harmful and toxic gases to the environment. Another major issue with microwave treatment of graphite is less absorption of microwave radiation by graphite ore. Also, the overall energy requirements are high and longer duration of treatment required. This method is a pretreatment process suggested before comminution or chemical treatment methods.

Gravity separation is a cheap, pretreatment method with the limited ability to reduce gangue. Advantages of gravity separation are no heating and absence of chemicals. However, space requirements for the gravity separator are too high. Despite low operating costs, huge capital

Table 4: Merits and demerits of different beneficiation techniques.

Beneficiation techniques	Merits	Demerits
Microwave pretreatment	(i) Selective and easy heating (ii) Energy efficient (iii) Environment-friendly output	(i) Low absorption of microwave (iii) Overall high energy requirement (iii) Longer processing time
Comminution	(i) Enhanced surface area (ii) Modifies particle-size distribution as per industry requirements	(i) Very low gangue elimination (ii) Can alter and damage particle shape (iii) Further processing is required
Flotation	(i) Cost effective (ii) Suitable for hydrophobic material (iii) Specific gangue removal is possible (iv)High purity output obtained up to 98%	(i) Multiple rougher/cleaner stages required (ii) Use of chemicals which might be hazardous
Gravity Separation	(i) Inexpensive (ii) Chemical free (iii) Low heating involved (iv) Large space requirement	(i) Less extent of separation (ii) High capital investments
Air Elutriation	(i) Easy segregation by varying air velocities (ii) Simple and easy maintenance	(i) Feed must have low moisture (ii) Low size particles input feed is unfavourable
Electroflotation	(i) Higher efficiency (ii) Faster bubble-particle interaction as compared to air bubble-particle interaction	(i) Complex process (ii) High electric supplies required
Ultrasound-assisted flotation	(i) High purity product obtained (ii) Release entrapped impurities	(i) Expensive (ii) Complex (iii) Less research done

investments are required in employing a physical method of beneficiation.

The most adopted beneficiation technique used is flotation. It is highly cost effective and a very well-suited method pertaining to hydrophobicity of graphite. It has the ability to reduce the gangue in the ore to a large extent. Specific gangue removal becomes easier depending upon the type and nature of gangue particles present in crude graphite ore with the help of depressants and conditioning reagents used. However, it requires multiple rougher/cleaner steps and few regrinding steps to obtain higher grade purity of the end product in the desirable size range. Also, use of chemicals is discouraged as it impacts the safety standards and releases residual pollutants which require further treatment. As compared to conventional flotation, electroflotation processes claim higher efficiency due to faster bubble (hydrogen and oxygen molecules are more active for hydrophobic material) and particle adherence over air-particle interaction which aids faster and better separation of ore from gangue. It is specifically more beneficial for low-grade graphite ores for extraction of ultra-fine graphite. However, the process is complex and has high electric supplies' requirements. Ultrasound-assisted flotation aims to release entrapped impurities and is beneficial if the objective is to produce a very high purity end product with preserved flaky nature of graphite.

Air elutriation helps in segregation of the graphite ore in the different size range by tweaking the air velocities. Cleaning and maintenance is simple and it outperforms traditional sieving techniques. However, wet feed is difficult to handle, and too low particle size of input feed cannot be processed.

12. Conclusions and Future Directions

12.1. Pretreatment Techniques. Pretreatment techniques for graphite flotation include "comminution" and "microwave pretreatment." They disintegrate the contaminants that are trapped in place to enable more effective grinding, and with the help of comminution, the product particle can be brought to desirable size range. Most effective grinding processes are stirred milling and jet milling.

For the treatment of middling, a moderate-speed ball mill and a flint pebble grinding medium are suggested. Delamination, when used as a way to regrind, can make coarse flake graphite with up to 98% fixed carbon.

It has been discovered that attrition milling works well for generating graphite flakes of smaller sizes while causing the least amount of form and shape degradation. Very less research has been carried out about microwave irradiation as it has the ability to eliminate nitrous and sulphurous gangue particles.

12.2. Froth Flotation and Flotation Reagents. Froth flotation is one of the most economical, energy efficient, and reliable beneficiation technique for graphite. The studies indicate that froth flotation, which outperforms acid leaching (keeping in mind environmental considerations), can make graphite samples with high purity and fixed carbon content of up to 98%.

Column flotation outperforms mechanical cell flotation when several cleaning processes are involved.

When selecting the reagents, special attention must be paid to the "Greenness Index." Ethers and polyglycols, such as Nasfroth 301 and Dowfroth 200, have been determined to represent the least environmental risk and to be extremely safe to handle. In addition, they have a higher flash point (195°C in the case of Dowfroth 200) and perform better than conventional industrial frothers like MIBC and pine oil. Despite the pine oil's lower flash point, Nasfroth 301 is superior to Dowfroth 200 according to HLB values.

Kerosene and diesel are hazardous to the environment, and hence their use is discouraged. A more effective collector reagent is Sokem 705C, an alcohol-ether mixture that is both environmentally friendly and economically viable. It has also been shown that IBM/07, a mix of terpenes and hydrocarbons, yield up to 96% fixed carbon and can be used as a collector in the graphite processing industry.

Sodium silicate and sodium cyanide are both acceptable inorganic depressants for siliceous gangue particles and pyrite, respectively. Organic polymers like starch are recommended to stabilise the pulp because of their steric effect.

New research for environmentally benign flotation reagents is vegetable oil (like soyabean oil) and biosurfactants produced by microorganisms which can be potential substitute for present day collectors.

12.3. Other Beneficiation Techniques. Air elutriation and flushing can be performed sequentially after the froth flotation procedure to obtain flake and amorphous graphite of the best quality, suitable for high market value. Electroflotation is suggested as a means of enhancing fine and ultrafine particle recovery which is difficult to be carried out by conventional flotation. To meet the increased demands of flaky graphite ultrasound-assisted flotation is a promising tool as it preserves the flaky shape and form unlike conventional grinding. One or more beneficiation techniques can be employed to get the desired benefits of different technologies.

Data Availability

Data are available from the corresponding author upon request.

Consent

The authors are responsible for the content and writing of the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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