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Technologies for processing of Barite: A conceptual review for use in Nigeria

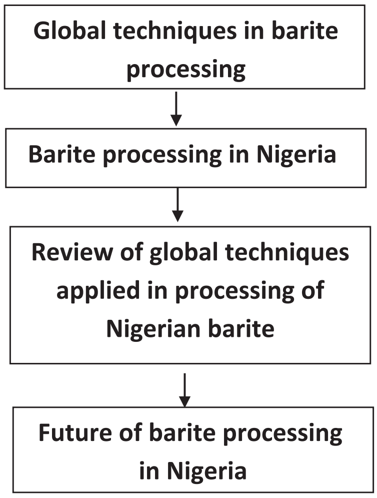
Utibe Benedict Edem✉, Oji Akuma, Ayoade Kuye, Joel Ogbonna Friday

Department of Chemical Engineering, University of Port Harcourt, Port Harcourt, Nigeria

HIGHLIGHTS

- Discussion of the physical, physicochemical, and chemical barite processing techniques.
- Review of current barite processing techniques in Nigeria.
- Economic feasibility analysis of improving the barite production in Nigeria.
- Future of barite processing in Nigeria.

GRAPHICAL ABSTRACT



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ABSTRACT

Barite ($BaSO_4$), an exceptional industrial mineral, has various applications based primarily on its physical properties. Over 80% of the world's barite is applied as a weighting agent in drilling fluids. Nigeria has an estimated reserve of over 20 million metric tons of barite ore scattered in different parts of the country, yet its oil and gas companies (IOC) lose over ₦5 billion annually in foreign exchange by importing barite. Presently, Nigrria's total national demand for barites is estimated at 10,000,000 tons per annum. The IOCs import barite because the locally produced barite has lower quality than the imported barite. Their argument is largely based on the fact that Nigeria's barite is often left unprocessed or processed using unconventional and ineffective techniques. Thus, the barite fails to meet globally acceptable specifications and standards required for drilling operations and other industrial applications. The Nigerian Content Development and Monitoring Board (NCDMB) has recently approved the implementation of a set of measures geared towards enforcing a ban on the use of imported barite and drilling fluids in the Nigerian oil and gas industry. Such measures are designed to bring Nigeria's barite to the required specifications and standards, increasing Nigerian IOC patronage of Nigeria's barite. The authors reviewed the present state of barite processing in Nigeria vis-à-vis globally acceptable processing techniques, with a view to applying them to Nigeria's barite.

✉ *Corresponding author: E-mail address:* edem_benedict@yahoo.com ; *Tel:* +23481-25736683

1. Introduction

The word barite is derived from the Greek "barys", which means "heavy; non-metallic mineral barite is unusually heavy with a specific gravity (SG) of 3-4.5 g.cm^{-3} in its pure state and is often referred to as heavy spar [1]. In its pure state, barite is generally white, white/milky, grayish, or colourless [2]. Barite crystals possess a symmetrical, tabular, prismatic, or bladed orthorhombic structure [3]. The crystal is interconnected by (SO_4) tetrahedrons, with Ba^{2+} linked among seven SO_4^{2-} tetrahedrons and connected with twelve oxygen ions and a coordination number of 12 [4]. Barite can be produced from primary barite deposits or other minerals containing barite as a gangue mineral [2]. Most often, barite processed from a primary mineral contains barite in a coarsely crystalline form, and it usually has a more or less intergrown appearance when associated with other ores and minerals.

Barite ore, which is non-magnetic in nature, possesses a refractive index of 1.63 and measures 3-3.5 on the Moh's scale of hardness. Furthermore, it is physically and chemically inert, possesses good stability, is non-toxic, acid and alkali-proof, possesses moderate rigidity, high absorption of harmful radiation, and is practically insoluble in all the usual chemical solvents (under ordinary conditions). The depth of occurrence, presence or absence of associated minerals, and the geographic location of the deposit affect barite ore quality [5]. Consequently, the quality of barite often varies in different locations within the same deposits. Barite consists of about 90% $BaSO_4$, with other associated minerals making up the remaining 10%. Krauskopf and Beiser [6] put the percentage of BaO and SO_3 at 65.70 % and 34.30 %, respectively. The associated minerals (often referred to as gangue minerals or impurities) are silicate, carbonate, iron oxide, sulfide, and clay origin include, celestine ($SrSO_4$), galena (PbS), sphalerite (ZnS), magnetite, pyrite (FeS_2), quartz (SiO_2), calcite ($CaCO_3$), dolomite (Ca, Mg(CO_3), marcasite (FeS_2), chalcopyrite ($CuFeS_2$), fluorite (CaF_2), siderite ($FeCO_3$), witherite ($BaCO_3$), feldspar ($NaAlSi_3O_8$), PbO_2, CdO, $A0l_2O_3$, CrO_3, CuO, TiO_2, $ZnSO_4$, ZnS, apatite and metal sulphides [7-11].

Barite ore can be classified according to the three principal associated minerals, quartz, iron, and fluorite, resulting in a single barite ore, i.e., quartz-barite ore and iron-barite ore classifications [12]. These gangue minerals, however, render commercial barite impure and lower its commercial value. One significant detrimental effect of gangue minerals within barite ore is a reduction in the specific gravity of the barite. This leads to another type of barite classification: a barite grade falling below 4.0 SG is classified as low-grade barite, whereas a grade between 4.2 and 4.5 SG is classified as high-grade barite.

Over 80% of barite is used globally as a weighting agent for drilling operations in the oil and gas industry [13,14]. This is because it increases the density of the drilling mud, is chemically inert, and maintains low solids, which results in the control of formation pressures, lowers production costs, and provides ease of handling [15,16]. The remaining 20% serves as raw materials in the production of several products, such as filler materials in paper, paints, rubber, glass, explosives, radiation shields, brake shoe linings, noise reduction engine compartments, spark-plug alloys plastics, and a source for barium-based chemicals and other types of chemicals [10,11,16-21].

Nigeria possesses a high reserve of barite. Various types of barite deposits can be found in nine Nigerian states, including Adamawa, Benue, Cross River, Ebonyi, Gombe, Nasarawa, Plateau, Taraba, and Zamfara [1,9,21-28]. The pink stars in Fig. 1 show barite mineral deposits in Nigeria [22,28]. In a detailed appraisal of Nigerian barite resources by the Nigeria Geological Survey Agency between 2005 and 2009, the barite reserves from eight states were estimated at 22,298,843 tonnes on an average vein depth of 20 m and a specific gravity of 4.2 g.cm^{-3} [22].

Since the primary source of revenue for Nigeria's economy is its oil and gas industry, barite is a crucial mineral for Nigeria's oil and gas drilling operations. Nigeria's national demand for barites is estimated at 10,000,000 tons per annum [7]. As earlier indicated, Nigeria has an estimated reserve of over 22,298,843 tonnes of barite ore scattered across the country [22]. However, despite Nigeria's substantial barite reserves, the IOC companies operating in the country largely depend on imported barite because locally-produced barite is of lower quality than imported barite. Multinational oil companies like Schlumberger, Halliburton, and Newpark are currently the major barite suppliers to Nigerian oil and gas companies at the rate of $300-400 per ton [29]. The importation of barite translates to a loss of over ₦5 billion annually in Nigerian foreign exchange [30].

In order to forestall the importation of barite, as well as insulate Nigeria from the present worldwide shortage of barite [31], the Nigerian Content Development and Monitoring Board (NCDMB) has currently approved the implementation of a set of measures geared towards enforcing a ban on the use of imported barite and drilling fluids in Nigeria's oil and gas industry. Such measures are designed to bring about optimal production and massive patronage of locally produced barite in Nigeria's oil and gas sector.

Accordingly, the current trend in Nigerian research and development (R&D) institutions is to design or apply suitable processing technologies to Nigeria's barite ore in order to make it meet global standards and serve as a viable substitute for imported barite in the oil and gas industry. Several studies

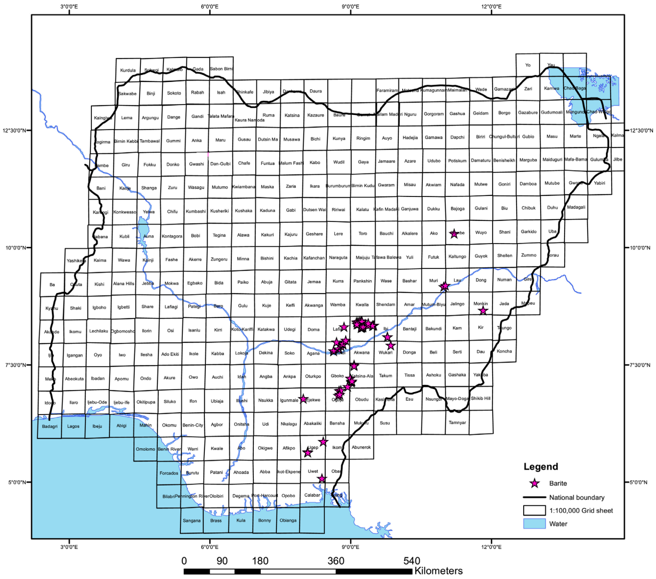

Fig. 1. Locations of barite mineral deposits in Nigeria [22,28].

on the processing of barite from Azara in Nasarawa State, Torkula and Kaseyo of Guma local government area of Benue State, Obubra in Cross River State, etc., have been carried out by researchers from Nigerian tertiary institutions as well as cooperate engineering bodies, such as the Nigerian society of chemical engineers (NSChe). For instance, Mgbemere *et al.* [29], Achusim-Udenko *et al.* [32], Nzeh and Hassan [33], Olugbemi [34], etc., have recently successfully carried out research aimed at tailoring Azara barite to meet global standards using well-proven tested methods.

2. Processing of barite

The use of barite for different applications requires varying barite specifications. However, the presence of associated minerals (impurities) produces low-quality barite, often resulting in a sub-standard barite ore that is unable to meet the required specifications for various industrial applications. To forestall this, low-grade Nigerian barite is usually processed to eliminate or minimise the impurities so as to upgrade it to meet the required quality for utilization in a particular application [35,36]. Several high-quality barite samples have been successfully processed from low-grade barite ores using various techniques [12,29,37-39]. The processing techniques employed in improving the quality of the barite depend entirely on the nature or grade of the ore, the type of associated (gangue) minerals, the gangue phases, the liberation degree of the minerals, and its liberation size [40].

Various forms of barite deposits exist, and each form strongly influences the processing technique employed, as well as the economics of the process [22]. Barite processing can be grouped under physical, physicochemical, and chemical techniques [41]. Established physical techniques include hand selection, gravity separation, magnetic separation, and electrostatic separation. Froth flotation is a widely used physicochemical process for barite processing, and chemical techniques include acidic, alkaline, and microbial leaching techniques, along with oxidation and oxidation-reduction separation. These barite processing techniques are discussed further in the following sections.

2.1. Physical processing

Physical processing techniques are better suited for ores that contain silicates, calcite, and iron as the principal gangue minerals [3]. The processes can be as simple as hand sorting and comminution operations comprising crushing, grinding, milling, desliming, and screening. However, the most widely used methods include gravity, magnetic, and electrostatic separation. Gravity separation (about the oldest method to separate minerals) is one of the two most commonly used methods. The other being the physicochemical method of froth flotation [35,42].

2.1.1. Gravity separation

Gravity separation is the primary sorting technique for barite ore worldwide and is generally applied to produce a better-quality concentrate grade (above 80%) [14]. Various CANMET studies have used the gravity separation technique and achieved about 90% $BaSO_4$, except for cases where low-grade feed was used [31].

Gravity separation techniques, which consist of jigging, tabling, spiral concentration, heavy media separation and desliming, are typically used for coarsely liberated ores when there is a high difference between the SG or particle size of the mineral and gangue phases. Gravity separation exploits differences in SG, fluid power, and mechanical forces to produce appropriate separation conditions to recover barite from its gangue minerals. For example, the gravity separation technique is the best method for upgrading the ore when quartz (SiO_2) is the main gauge mineral in the barite ore deposit. However, it should be noted that even though the cost of gravity separations are low, the concentrate recovery is equally low. In Hengnan province, China, barite ore separated from quartz using the gravity separation method resulted in a barite concentration of over 84.05% $BaSO_4$ and a recovery of 87.85% [12].

In Algeria, the gravitational separation technique used on barite from both Ain Mimoun and Bou Caid mines produced concentrate that does not meet the quantity or quality requirements of certain consumers (pharmaceutical, chemical products, etc.) due to the loss of $BaSO_4$ (a useful mineral) and the presence of gangue impurities. Consequently, Batouche *et al.* [43] proposed in-depth research into the physio-chemical and mineralogical characterisation of the barite with the aim of finding an adequate processing technique to obtain a high-grade barite concentrate. Gravity separation research has also been carried out to discover organic dense media (acetylene tetrabromide or tetrabromethane) that would ensure efficient separation of barite. Gravity separation also includes jigging, spirals and table operations. The various gravity techniques applied from litreture as discussed below.

2.1.1.1. Jigging

Jigging is used to separate barite from other rocks and minerals using jigs. Jigs use pulsating water to separate barite from the waste by gravity. The feed must be crushed finer than a predetermined liberation size, namely a size that liberates the barite from the waste. The feed size also must be a size that the jig can handle. The pulsating water lifts the feed material, allowing the heavy barite to sink to the bottom. The lighter waste stays at the top and is washed off at the end of the jig. In some cases, jigs are used in series to upgrade the material further. Therefore, there must be a difference in the specific gravity between the waste product and the barite for this method to work. A size range of –355 to +250 μm is believed to be ideal for the jigging operation [44]. An interesting comparison between wet and dry jigging was demonstrated in a study of several barite ores from Nova Scotia [40].

2.1.1.2. Spirals and tables

Tabling and spiraling are used to recover fine-grained barite [40]. Spirals and tables are used infrequently because of the considerable cost of operating the units. Both methods use specific gravity and material movement to separate the waste from the ore.

2.1.1.3. Heavy medium separation

Heavy-media separation, like jigging, is usually employed to recover coarse-grained barite from high-grade barite ore. Therefore, heavy media separation is normally adopted for high-grade and coarsely liberated ores, while other gravity techniques are used to produce intermediate concentrates [12].

2.1.1.4. Desliming

Desliming is a common procedure performed in mineral processing primarily to eliminate fine particles (slime particles) that consume excessive amounts of collector because of their large surface areas and coating of valuable minerals, which hinders the bubble-mineral contact [45]. After milling the ores, fines in the milled products and secondary sources, such as tailings, increase reagent consumption and metal recovery during froth flotation, which usually proceeds desliming. Hence, the removal of such slimes is necessary to decrease reagent consumption and improve metal recovery of the physicochemical process known as froth flotation (which normally proceeds desliming).

2.1.2. Magnetic separation

When iron oxide is found in association with barite, it is easily separated by the magnetic separation technique [46]. Magnetic separation is used to remove iron-bearing minerals in barite using the magnetic differences between barite and iron oxide minerals to obtain a high-grade barite concentrate. It is an important process in producing barite compounds that require low iron, such as barium drugs. In magnetic separation, reagents (manganese stearate and manganese oleate) have been developed to selectively render the surface of certain minerals magnetic, making it easy to separate the magnetic minerals from the non-magnetic minerals. Jakabsky *et al.* reviewed techniques for improving the magnetic properties of minerals prior to magnetic separation and discussed factors affecting the adsorption of fine magnetite onto the particle surfaces due to the physicochemical properties [47]. Another study concluded that the factors affecting the selectivity of the magnetic coating process vary from those of other mineral separation techniques [48]. During their magnetic separation experiment, it was noted that barite in calcite/barite ore had a magnetic recovery of 8.6%, while it had a non-magnetic recovery of 91.4% at a particle size of -150 to +75 microns, using sodium oleate, Na_2SO_4, pH = 9, and $NaClO_4$.

2.1.3. Electrostatic separation

The electrostatic separation technique exploits the differences in conductivity between different minerals to achieve separation [49-52]. Electrostatic separation techniques are typically only used when alternative processing techniques will not suffice, as the comminution steps in mineral processing flowsheets are generally wet processes, and the energy requirements to drive off all moisture prior to electrostatic separation can be significant [50]. Unfortunately, all electrostatic separation techniques (drum-type, belt-type, plate-type, etc.) require that the feed material must be completely dry [53]. The energy costs associated with completely drying ground ore prior to an electrostatic separation step are likely prohibitively high for the industrial-scale application of such a process. Electrostatic separation technology has been used to separate conducting minerals from non-conduction minerals such as barite/quartz [52,54]. Electrostatic separation was used to separate barite from quartz using positive polarity, achieving a concentrate of 84.1% $BaSO_4$ [52].

2.2. Physicochemical processing

2.2.1. Froth flotation

Froth flotation is one of the most widely used barite processes. By definition, froth flotation is an electrochemical process in which mineral surfaces react with reagents in a solution to form hydrophobic complexes that impart flotability to the mineral particles. It was used to significantly improve the barite concentrate grade in depositional barite ore, sulfide ore, and fluorite-associated hydrothermal barite ore [40,56]. Like gravity separation, froth flotation is the best method for upgrading the ore when quartz (SiO_2) is the main gauge mineral in the barite ore deposit. It is used to liberate barite from its associate minerals in very fine-size fractions and high-grade concentrates [7,12,14]. Normally, the feed for a flotation cell is 40 mesh or finer. However, unlike gravity separation (applied to recover coarse-grained barite), fine-grained barite is recovered from complex or complicated ore composition using froth flotation. In other words, it is used when the liberation size is finer than what a jig or other equipment can handle. Froth flotation is more interactively applied in industries than other processing techniques. The separation process, which takes place in a mineral-water slurry system, is achieved based on differences in physicochemical surface properties of the individual mineral constituents, particularly the wettability of water [57]. The surfaces of selected minerals of finely ground ores are made hydrophobic (water-repellent) by conditioning them with suitable selective reagents. The specific hydrophobic mineral particles attach to rising air bubbles introduced into the pulp and are carried to a froth layer above the slurry, separating from the hydrophilic (wetted) particles that remain submerged in the pulp [58,59]. Chemical reagents, namely collectors, depressants, and pH modifiers, are applied to separate the selection group of minerals adhering to the air bubbles while depressing the unwanted associated minerals. A schematic diagram of a froth flotation cell is shown in Fig. 2.

According to Denga *et al.* barite flotation can be carried out by either reverse or direct flotation [61]. Reverse flotation involves removing base metal sulfides or pyrite, thus leaving concentrated barite in the tailings, which is then recovered by flotation. Flotation of barite from ores containing fluorspar, silicates, and rare earth oxides (REO) is called direct flotation.

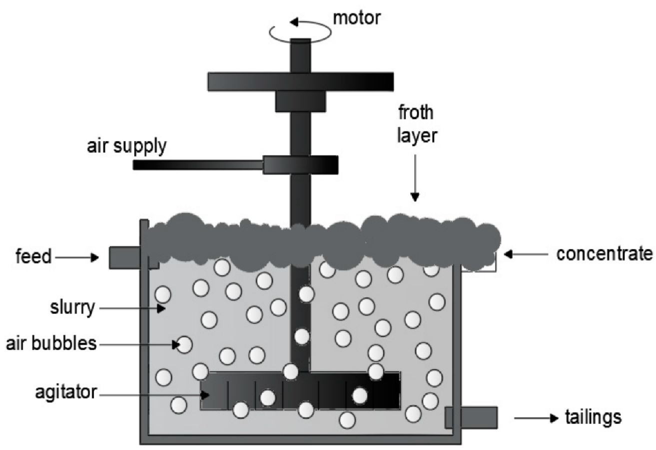

Fig. 2. Schematic diagram of a froth flotation cell [60].

The process of flotation involves the use of collectors to attach the minerals to air bubbles that help raise them to the surface, as well as the use of a depressant to prevent unwanted minerals from floating. The ore particle flotation usually begins with the addition of a depressant, followed by the collectors. Commonly used collectors include fatty acid alkyl sulfate, sodium oleate, oleic acid, oleic acid alkyl sulfonate, oxidized paraffin soap, tal oil, and hydroxy acid ester. Sodium silicate and fluoride acid sodium are two major depressants used in barite flotation. Sodium silicate is usually used as a depressant for quartz, silicate, and aluminum silicate minerals, while fluoride acid sodium is used to depress feldspar, serpentine, tourmaline, quartz, and other silicate minerals during flotation. In conjunction with sodium silicate, a pH modifier, such as sodium carbonate, can adjust and improve the selectivity of the sodium silicate depressant on different barite grains. Adding sodium carbonate to the barite flotation process can also improve the whiteness of barite. The solubility and electrophoretic mobility of these reagents have been studied in recent times [10]. Also, several cheap and environmentally friendly reagents have been developed to improve the flotation efficiency of separating valuable and gangues minerals [62]. For instance, acidified water glass (AWG) has been proven to be an effective depressant in separating barite from calcite using NaOl as the anionic collector [61]. Fig. 3 gives the schematic diagram for the flotation separation of barite from calcite with AWG as a depressant and a NaOl collector at a pH of 8.

Previous research has been focused on direct flotation using oleic acid/oleate as anionic collectors. Generally, while oleate produces high-grade concentrates, it is usually unacceptable for drilling applications because the oleate absorbed by the surface of the barite disturbs the settling characteristics in the thickeners, leading to air entrainment and lowering the specific gravity of the drilling mud [10]. The absorbed oleate can be removed by heat treatment. However, it is both

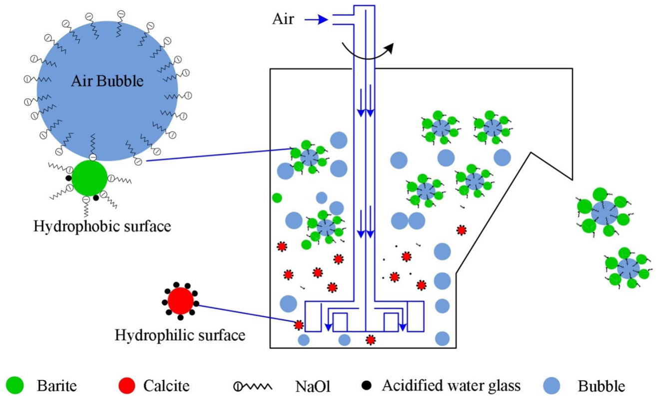

Fig. 3. The schematic diagram for flotation separation of barite from calcite using depressant AWG and collector NaOl [61].

technically difficult and expensive. Hence, the reverse flotation technique, wherein silica, silicate, and other minerals are floated using fatty amines as cationic collectors, is considered a better option. Further, it is advantageous to separate silica with approximately 11% instead of barite. Since silica is negatively charged, cationic reagents are the most suitable as collectors [10]. Reverse flotation has also been used in the processing of low-grade barite dumps interlocked with gangue minerals using an amine collector to avoid the collector coating the barite surface [63]. In that study, reverse or indirect flotation, using varied particle sizes and pH values, was applied to purify Kiana barite ore, and oleic acid, corn starch, and corn oil were used as the collector, depressant, and frothier, respectively. The froth flotation process resulted in a specific gravity of 5.0 and an increased $BaSO_4$ content from 91.16% to 92.26% at an optimum particle size and pH value of 300 µm and 7, respectively [63].

Using the principle of froth flotation, barite samples with high concentrations of $BaSO_4$ have been recovered from different sources. Table 1 gives some previous investigations on upgrading barite using froth flotation.

2.3. Chemical processing

The aim of chemically processing barite is primarily to remove Ni, Fe, Ti, C, Mn, Ni, and other colouring elements capable of impeding barite ore from achieving the whiteness criteria in chemical industries, where "colour" is pertinent. It is also applied in other industries where barite processing is required. The primary technique applied in the chemical processing of barite is leaching. Chemical leaching can be achieved using acid or alkali; hence, the terms acidic and alkaline leaching. Hot water can also be used in leaching [31]. Oxidization, oxidation-reduction reaction, and thermal reduction are other forms of chemical processing. Brief reviews of these techniques follow next.

2.3.1. Acidic-leaching

Acidic leaching is one of the best-known and most widely employed chemical processes for obtaining an estimation of 90%. With regards to acid treatment, most industries employ conventional inorganic acids, such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), hydrogen fluoride (HF), and nitric acid (HNO_3), for the preparation of highly pure barite used in the production of paint, ceramics, glassware, paper, etc. These reagents dissolve and remove the metal oxides and other insoluble impurities attached to barite, separating the barite from valuable minerals. However, the presence of adhering chemicals and the elimination of water-soluble salts Na, K, Ma, and Ca resulting from acidic leaching poses a major environmental concern [13].

Acid leaching is also used to process complex sulphide

Table 1. Previous investigations on upgrading barite using froth flotation [62].

Collector	Depressant or modifier	pH	Recovery (%)	Grade	Reference
Sodium oleate (700 $g.t^{-1}$)	Water glass (500 $g.t^{-1}$)	8	80.71	98.21	Zhao *et al.* [64]
Sodium oleate (800 $g.t^{-1}$)	Sodium silicate (500 $g.t^{-1}$)	8	92.5	91.5	Zhao *et al.* [64]
Oleic acid (800 $g.t^{-1}$)	Sodium silicate (2000 $g.t^{-1}$)	9	9	93.24	Raju *et al.* [40]
Palmitic acid (0.01 $mol.L^{-1}$)	Sodium silicate	10	85	91.1	Achusim Udenko *et al.* [32]
Sodium oleate (800 $g.t^{-1}$)	Sodium silicate (500 $g.t^{-1}$)	9	91.94	96.32	Wang *et al.* [14]
Sodium dodecylsulphate	Citric acid-Potassium dichromate	6	99	97.3	Ciccu *et al.* [65]
Aero 845	Sodium silicate	9	-	65.9	Harris [66]
Petroleum sulfonate (1000 $g.t^{-1}$)	-	6	89.4	95.1	Krauskopf and Beiser [6]
Petronate L (1000 $g.t^{-1}$)	-	6.5	87.4	93.4	Kecir M. and Kecir A. [9]
Sodium dodecylsulphate (5-10 M)	-	10	80	99	Ślączka [67]

barite ore using a ferric chloride solution at temperatures between 80 to 150 °C [68]. In one study [69], complex sulphide-barite ore was leached by a ferric chloride mixture, with the optimal results obtained at a leaching temperature of 100 °C. Their results confirmed the possibility of directly processing the complex barite ore using chemical methods such as acidic leaching.

2.3.2. Alkali-leaching

Like acid leaching, alkaline leaching is an effective route to increase the barite concentration. NaOH and Na_2CO_3 are commonly used reagents employed to dissolve silicate and other carbonate gangue minerals associated with the barite ore.

2.3.3. Oxidation

The oxidation technique primarily involves the use of common oxidants, such as H_2O_2, $KClO_4$, KNO_3, etc., to oxidise and dissolve associated coloured impurities from low valence to high valence during the process so as to improve whiteness.

2.3.4. Oxidation-reduction

The oxidation-reduction method involves dissolving the oxide and impurities first, especially Fe, and then converting Fe^{3+} to Fe^{2+} using reducing agents, such as $Na_2S_2O_4$, to remove the coloured impurities. This improves the whiteness and conforms to the criteria of the relevant industry.

Table 2 gives the outlines the various processing techniques applied along with their respective principles.

Based on the literature, a combination of several processing techniques is usually required to purify barite. Barite processing using a combination of methods can improve the barite grade quality commensurate with global standards. For instance, the barite and fluorite minerals found in Eskisehir-Beylikahir, Turkey, were investigated using a combination of gravity concentration, flotation, and high-density magnetic separation operations to recover barite and fluorite [70]. Their results produced a barite concentration assaying 87.45% $BaSO_4$ with 49.61% recovery using a combination of gravity concentration-flotation-magnetic separation offered the best results. Their flotation process used 900 $g.t^{-1}$ S3903 as a collector and 1250 $g.t^{-1}$ Na_2SiF_6 as a depressant. A high-grade barite concentrate was produced from complex iron ores containing limonite, hematite, and siderite in Krerrtikovrzi, Bulgaria [37]. High-intensity electromagnetic wet separation and flotation were employed. In that study, collecting flotation agents OMC 199 and AERO 8-15 (2:1 ratio) at a total dosage rate of 400 - 450 $g.t^{-1}$, and waterglass was used as a silica depressant at the application rate of 4 - 4.5 $kg.t^{-1}$. Results indicated that high-grade barite concentrate, assaying 97-98 wt%, was obtained [37]. Using flotation and leaching, barite ore from Duddar Area, Pakistan, containing 76.04 wt% $BaSO_4$ obtained a barite concentrate of 98.86%, with the final barite concentrate conforming to the specification of industrial-grade barite [10]. Deniz and

Table 2. Processing techniques and their respective principles (modified from [31]).

Processing methods	processing principles	Application
Gravity concentration	The density difference between barite and associated minerals. For coarse particles.	includes washing, desliming, screening, jigging, shaking, and other process methods used for residual ore
Flotation technique	The difference in the physic-chemical properties of the surface of barite and associated minerals. For fine particles.	commonly used in sedimentary barite deposits and associated hydrothermal barite ore, such as sulfide ores and fluorite
Magnetic separation	The difference in magnetic properties between barite and associated minerals.	mainly used to remove the iron oxide-based impurities from the barite ore or when there is a high concentration of iron in the structure of barite
Acidic/alkaline leaching	Increases its specific surface area and pore volume to improve its adsorption capacity for impurities.	metal oxides, sulphides, silicate, and carbonate
Oxidation	Changes oxidants to oxide and dissolve associated colored impurities.	coloured impurities
Oxidation- reduction	Dissolves the oxide and impurities and then converts impurities using a reducing agent.	metallic oxides

Guler applied dry/wet high gradient magnetic separation (HGMS) and bleaching methods to investigate the rejection rate of colouring impurities from barite ore with the aim of increasing the brightness index of the barite concentration [55]. Their results showed a substantial enhancement in the product quality using sulfuric acid leaching at 10% acid concentration for 30 min. However, colouring impurities could not be eliminated enough to obtain a marketable product. On the other hand, bleaching using hydrochloric acid (HCl) gave a significant result; barite of marketable properties was obtained by applying bleaching at 15% HCl concentration for 15 minutes. Processing investigations on barite revealed that using wet HGMS, followed by HCl bleaching, increased the brightness index of barite from 68.05% to 90.12% [55].

3. Current advances in barite processing

Recent research has seen great advances in the use of several processing technologies to improve the separation efficacy of barite from its associated gangues minerals.

Kolawole *et al.* reports a recent development in the use of reagents (manganese stearate and manganese oleate) to achieve magnetic separation by selectively rendering the surface of certain minerals magnetic, thereby making it easy to separate the magnetic minerals from the non-magnetic minerals [31]. In the case of gravity separation, research has discovered organic dense media (acetylene tetrabromide or tetrabromethane) that will ensure efficient separation of barite from its unwanted mineral(s).

Cost-effective technologies such as using biomass and microorganisms in bio-processing have also advanced. In froth flotation, cheap and environmentally friendly reagents have been developed to improve the separation efficiency between valuable and gangues mineral(s) [59]. Additionally, biomass macromolecules that can hydrate in aqueous solution and be more selectively adsorbed on the gangue minerals are being developed, making them potential depressors in non-sulfide ore flotation. In this regard, biomass has reportedly been used to separate barite from its gangue mineral by applying froth flotation [31]. According to Gahan *et al.* [71], a reasonable degree of success has been achieved in the bioleaching of barite on a laboratory scale; however, several aspects of the study, such as scaling up this laboratory experiment into full-scale plant operations and optimising the engineering aspects of the research require further research.

While studies have shown that the bio-modification of surfaces of minerals, such as barite, involves the complex action of microorganisms on the mineral surface, the mechanism of bacteria adsorption and the surface reactivity remains relatively unknown. The bio-flotation and bio-flocculation processes are a mineral response to the bacterium's presence, which is essentially the interaction between the physicochemical properties of the mineral surface and the microorganism. The physicochemical properties of the mineral surface include its atomic and electronic structure, the net potential, the surface wettability, and the acid-base properties. However, it is vital to expand our fundamental knowledge of microorganisms in order to better govern the seemingly effective solutions offered by the rapid biotechnological advancement in natural resource processing technologies [72].

4. Barite processing methods in Nigeria

For Nigeria's barite to meet global standards/specifications and be commercialised, it is essential to process it using successful, globally acceptable techniques. The prevalent (applicable in Nigeria) method of blending low-grade barite with local or imported high-grade barite in order to meet the API requirement of 4.2 is unacceptable [11,73], primarily because it fails to address the issues of impurities that are detrimental to the end-product.

Small-scale barite processing is also carried out using other non-conventional methods in Nigeria. Here, the barite ore is subjected to washing and comminution, after which it is heated to temperatures between 1100-1200 ^{o}C. The resulting barium sulphate, often referred to as black ash, is composed of roughly 80-85% barium [31]. The black ash is then leached with hot water and filtered to recover the barite from the ores. Next, barium sulphate is precipitated from the leached solution using sodium sulphate. The final steps involve filtering, washing, drying, pulverizing, and packaging the white precipitated barium sulfate [74]. Although this method goes a step further in addressing the separation of impurities in the form of gangue mineral from the barite ore, it is limited to small-scale barite production and falls short of tested global methods in achieving the required specifications for barite application in drilling operations [31].

Thus, it is necessary to apply globally tested processing techniques to successfully process barite ore. The processing and economics of these methods are often determined by the various classifications of barite deposits.

4.1. Review of modern processing techniques for Nigerian barite

Only a few up-to-date studies have been carried out on the use of globally acceptable processing techniques for Nigeria's barite ores. For example, Ibisi used a combination of magnetic separation and flotation (n-acetyl sulphate as a collector at a pH of 10.8) to investigate the mineralurgical composition and thermal behaviour of a barite sample from Nigeria, achieving a $BaSO_4$ concentrate of 96.8 wt% [75]. Barite ore samples from Azara in Nassarawa State were processed using both jigging and magnetic separation processes using an atomic absorption spectrophotometer to analyze the elemental composition [32,76]. The elemental composition results showed that the $BaSO_4$ content using both methods was 98%. Further comparison between jigging and magnetic separation processes showed that the former produces a more satisfactory result. A combination of gravity and electromagnetic processes of a barite vein deposit in Tunga produced an average specific gravity ranging from 3.16 to 4.24 $g.cm^{-3}$, an increase from the 2.63 value recorded by the host sandstone rock [77]. Nzeh and Hassan conducted laboratory-based research that combined jigging, tabling separation, and leaching (with HCl and H_2SO_4) on Azara barite [33]. The process increased the specific gravity of the barite from 3.85 to 4.46 $g.cm^{-3}$. Mgbemere *et al.* studied the jigging, froth flotation, and chemical leaching of an Azara barite with a particle size of +180 μm, (−180 to +90) μm using pine oil, oleic acid, HCl, and HOCl [29]. Leaching was introduced because an initial study's chemical analysis indicated that the amount of silica still present in barite was still very high after the froth flotation. Results showed an increase in the specific gravity of Azara barite ore to 4.38 $g.cm^{-3}$ from an initial value of 3.27 ± 0.03 $g.cm^{-3}$, while the $BaSO_4$ concentrate rose from an initial value of 64.6% to 99.5% $BaSO_4$. Research findings also showed the elimination of water-soluble salts, Ca, Mg, Na, and K, needed for both the rheology specification of drilling fluid and filtration control in drilling applications. Further laboratory-scale experimentation on Azara barite by jigging and froth flotation of (−350 to +180) μm using NaOH and oleic acid resulted in an increased barite specific gravity from an initial 3.72 to 4.23 $g.cm^{-3}$ with a recovery of 92.9% $BaSO_4$ at a pH value of 7; however, at a pH value of 3, the specific gravity value dropped to 3.78 $g.cm^{-3}$ [29].

4.2. Economic feasibility analysis of barite processing in Nigeria

Flotation and gravity separation are the two most common methods used to process Nigeria's barite. However, their applications have been largely restricted to laboratory-scale research, with little mention of commercial or industrial-scale processing. According to Nwozor and Chukwunenye, the few processing plants in the country produce a little above 40,000 metric tonnes per annum, creating a huge supply gap that is presently bridged by the massive importation of this essential product [2]. The limited scale-up of the process to industrial and commercial scale, or the construction of pilot processing plants in Nigeria, is partly due to the long-held belief (primarily by the IOC's operating in Nigeria) that investment in processing Nigeria's local barite is unfeasible or commercially unproductive.

However, the economic feasibility, viability, and profitability of a commercial-scale barite processing plant in Nigeria remains unquestionable. Nwozor and Chukwunenye's study showed that a crusher with a 75 metric tonnes per hour capacity, at a market price of ₦40,000 per tonne of processed barite, and a medium-scale plant evaluated at an annual capacity of 142,000 metric tonnes could generate a profit of in the range of ₦3.6 billion at 60% capacity utilisation (representing the commissioning year). Moreover, Eze formulated an economic model to determine the economic feasibility of commercial barite production in Nasarawa State, Nigeria [78]. The specific aim of the model was to ascertain if an investment in commercial barite production in Nasarawa is attainable and profitable within an estimated cost. The model assumed capital and operating costs and input data were barite projected annual production price, royalty, price, and mineral taxes. Payout Period, internal rate of return (IRR), and the net present value formed the output data on which the economic decisions were made. The economic analyses showed a payback period of roughly four years, along with an IRR value of 28% and an NPV of USD 1.36 million using a 10% discount rate, confirming that an investment in commercial barite production in Nasarawa state is both feasible and profitable. Such analysis should be extended to the Cross River and Taraba states, where barite is also available in commercial quantities. More recently, a barite plant was reported to have been established in Ugaga, located in the Cross River state. This plant is expected to harness the potential of the barite processing industry in Nigeria, enhancing economic growth and promoting local development in the sector [79].

4.3. Future of barite processing in Nigeria

The future of barite processing on an industrial scale in Nigeria is optimistic. Nigeria is one of the largest oil-producing countries in the world, with an estimated reserve of over 22 million metric tons of barite. With the ban on barite importation, there is a potential business in barite production to increase the country's GDP. Government policies pertaining to barite (and mineral resources as a whole) have both energized and incentivized scholars and industrialists to undertake present-day barite processing methods capable of meeting the barite demands of its oil and gas industry. Furthermore, with the setting up of the mining cadastral office, as well as enacting relevant mining laws, investors have been encouraged to participate in the production of barite by partnering with existing title-holders or outrightly obtaining titles to improve the production output using cost-effective mining technology, especially in areas where the barite vein lies at 20 m or less.

5. Conclusion

Barite processing techniques strictly depend on the nature of the ore, the type of gangue associated with the minerals, and the liberation size of the minerals. Processing low-grade barite using the correct technique(s) can improve the specifications/standards of barite to meet global standards. This paper discusses techniques such as flotation, gravity separation, magnetic separation, electrostatic separation, and leaching from a global point of view.

Nigeria has a deposit of approximately 20 million metric tons of barite but is still importing far more barite than it produces. Furthermore, its barite is usually used unprocessed or processed through non-conventional methods, resulting in barite that fails to meet globally acceptable specifications/standards for various industrial uses.

Current research in the processing of Nigeria's barite was discussed in this paper. Flotation and gravity separation remain the two most common methods used to process Nigeria's barite.

6. Recommendation

It is imperative for researchers to carry out sufficient research on different techniques to process Nigeria's barite in order to bring Nigeria's barite up to industrially acceptable specifications/standards. Additionally, present laboratory-scale research on Nigeria's barite using global processing techniques should be converted into a commercial-scale operation, with the engineering aspects of the research fully optimised. This will effectively help stop the annual loss of over ₦5 billion in Nigeria's foreign exchange caused by barite importation, as well as insulate Nigeria from the present worldwide shortage of commercial barite. Furthermore, separation methods (other than gravity separation and flotation) should be explored for Nigeria's barite to ascertain their effectiveness in processing Nigeria's barite. Research on cost-effective and environmentally friendly barite processing techniques, such as bio-processing (using biomass or microorganisms), should be equally applied to Nigeria's barite.

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Additional information

Correspondence and requests for materials should be addressed to U. B. Edem.

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