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Barite processing for industrial use – A bibliographic survey

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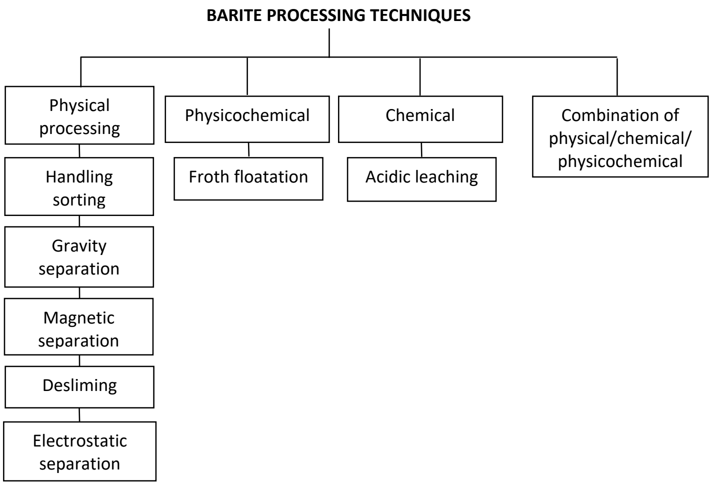
HIGHLIGHTS

- Barite processing is vital for several chemical end products and petroleum applications.
- Barite processing can be achieved using physical and chemical techniques.
- Physical processing techniques include hand sorting, conventional gravity concentration, magnetic separation, desliming and electrostatic separation.
- Physicochemical separation techniques include froth flotation, chemical separation operation, acidic leaching, and combination of processing techniques.

GRAPHICAL ABSTRACT



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ABSTRACT

Presented here is a bibliographic survey, which covers the work done in the period ranging from 1912 to 2023 on the various techniques employed in the processing of barite, along with the results obtained. This paper, the outcome of thorough research on various literature available from earlier studies, serves as a compendium of the major areas summarised in one paper. However, the objective of this paper was not to critique or review the outcomes of the various researchers. This article, which is essentially a one-stop guide handbook, will introduce the processing techniques used in barite processing, report the various research carried out by previous researchers using globally accepted processing techniques, and state the critical findings during the period under review.

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1. Introduction

Barite ($BaSO_4$), as an important industrial mineral, has various applications based on its physical and chemical properties. The crystal structure of barite can be represented as shown in Fig. 1. As seen, the crystal is characterised as a rombi cholohedral, like other sulfides, revealing a microstructure of almost regular tetrahedrons with O-atoms on the corners and S-atom at the center; hence, barite crystals possess a remarkably symmetrical, tabular, prismatic, or bladed orthorhombic structure [1]. The crystal is interconnected by a SO_4 tetrahedron, with seven SO_4^{2-} tetrahedrons linked by Ba^{2+} and connected with twelve oxygen ions and a coordination number of 12 [2].

Barite consists of about 90% $BaSO_4$ plus other associated minerals, making up the remaining 10%. The presence of the associated minerals, the geographic location of the barite deposit, and the depth of barite occurrence affect the quality of barite, which further affects its end uses, as different barite products require varying properties [3].

The associated minerals include quartz, calcite, dolomite, fluorite, clay, iron, etc. These minerals are often associated with bartyte in the form of celestine ($SrSO_4$), galena (PbS), sphalerite (ZnS), magnetite, pyrite (FeS_2), quartz (SiO_2), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)$), marcasite (FeS_2), chalcopyrite ($CuFeS_2$), fluorite (CaF_2), siderite ($FeCO_3$), witherite ($BaCO_3$), feldspar ($NaAlSi_3O_8$), PbO_2, CdO, Al_2O_3, CrO_3, CuO, TiO_2, $ZnSO_4$, ZnS, apatite, and metal sulphides [4-7].

Over 80% of barite is used as a weighting agent for drilling mud production in the global oil and gas industry. This is because barite increases the density of the drilling mud, is chemically inert, and maintains a low solids presence. These properties ultimately result in the control of formation pressures in the well borehole, reducing production costs and increasing ease of handling [8,9]. The other 20% serves as a feedstock in the production of several chemical products such as rubber, glass, alloys, plastics, paint, filler materials in the production of paper, pharmaceuticals, radiation shields, noise reduction engine compartments, brake shoe linings, spark-plug, as well as a feedstock for several barium-based chemicals and other chemical types [5,6,9,10-14].

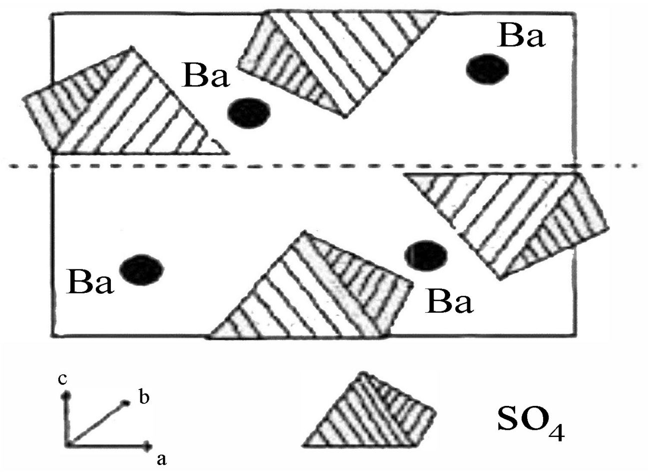

Fig. 1. The crystal structure of barite.

Over the years, several studies have been conducted on barite ore processing technologies to make them more acceptable for various industrial uses. These technologies are primarily aimed at eliminating the minerals associated with barite ore in order to bring barite properties to acceptable specifications/standards required for its primary use in the formulation of drilling mud and for its secondary use as a feedstock for the production of a wide variety of barite-based products. If left unattended, these impurities can have deleterious effects on essential specifications required for the successful applications of barite.

Before initiating barite processing, it is necessary to analyse the physical, physicochemical, and chemical properties of the barite ores mineral in order to determine the specific method for processing.

The processing technologies can be physical, physicochemical, or chemical in methodology. Physical methods considered in this research include hand sorting, gravity separation (jigging, table shaking), magnetic separation, electrostatic separation, and desliming. The physicochemical separation techniques were limited to froth flotation, and acidic and alkaline leaching were the two chemical separation techniques surveyed in this research.

The remaining processing technologies have been divided into the following categories described in more detail in the following sections:

1. Physical separation techniques, including hand sorting; conventional gravity concentration (CGC) or jigging, table shaking, and spiral concentration; magnetic separation; desliming; and electrostatic separation.
2. Physicochemical separation techniques, including froth flotation, chemical separation operation, leaching (acidic and alkaline leaching), and a combination of processing techniques.

2. Physical operations

2.1. Hand Sorting

Hand Sorting takes advantage of barite-associated mineral colour, density, and other visible differences to separate barite from its associated gangue mineral(s).

Huang *et al.* [15] posited that the hand sorting method is simple and easy to operate as there is no need for large-scale equipment and reagents. However, production efficiency is very low, and human resources and time are severely wasted.

2.2. Gravity separation techniques

Gravity separation techniques, which consist of dense or heavy media separation, jigging, shaking tables or tabling processes, and spiral concentration, use the differences in specific gravity (SG) between the ore and its associated mineral(s) to achieve separation. Heavy-media separation and jigging are most suitable in the recovery of coarse-grain barite ore, as opposed to table shaking, which is most suitable for fine-grained barite recovery [16].

For example, Çifiçi and Kumuru applied the shaking table method on complex ore samples containing barite [17]. A barite concentrate of 85.5% BaSO4 with a 43.75% recovery rate was obtained. Andrews and Collins used tabling and spiral concentration to successfully recover fine-grained barite from its associated minerals [16].

Yüce *et al.* applied tabling to a complex ore containing 32.2% $BaSO_4$ to obtain a barite concentrate of 85.5% $BaSO_4$, with a 55.8% recovery [18].

Huang *et al.* found that the effectiveness of gravity separation in removing impurities from barite with high specific gravity results in a barite concentration grade of over 90% [15]. Wang *et al.* separated barite ore from quartz using the gravity separation method, resulting in a barite concentration of over 84.05% $BaSO_4$ and a recovery of 87.85% [19]. Batouche *et al.* applied the gravitational separation technique in Algeria's Ain Mimoun and Bou Caid mines [20]. Results showed that the barite concentrate obtained (quantity and quality) does not meet the various set points of specific parameters required to produce globally acceptable end-products for several pharmaceutical and chemical products. This is primarily because of the loss of $BaSO_4$ (a useful mineral) and the presence of gangue minerals or impurities after the use of gravitation separation techniques. Consequently, Batouche *et al.* recommended that in-depth research of the physicochemical and mineralogical characterisation of the ore be conducted to find the adequate processing technique(s) to obtain a high-grade barite concentrate.

Nzeh and Hassan used a shaking table in the processing of barite to remove the gangue minerals associated with the ore [21]. Results showed that the method was very effective in removing impurities/gangue minerals and, thus, recovery of barite with high specific gravity for the formulation of drilling fluid for use in oil and gas exploration. Kolawole *et al.* reported that the Canada Centre for Mineral and Energy Technology (CANMET) applied gravity separation to achieve roughly 90% $BaSO_4$ [22]. The researchers also emphasised that studies have been done to discover organic dense media (acetylene tetrabromide or tetrabromethane), ensuring efficient separation of barite through gravity separation.

Nzeh and Popoola applied two forms of gravity concentration methods, namely, jigging and table shaking, to ascertain the effectiveness of each process in the recovery of barium from its ore deposits in Azara-Nassarawa, Nigeria [23]. Its effectiveness as a drilling fluid in oil and gas operations was further analyzed using its specific gravity as the primary determinant. The raw barite sample was composed of an initial value of 36.2% BaO and 40.5% Ba, respectively, with a specific gravity of 3.85. Applying jigging and table shaking resulted in a barium concentrate recovery of 130.98% and an increase of specific gravity to 4.28, while using table shaking resulted in a barite concentration recovery of 89.81% and a specific gravity increase to 4.18. Thus, the values obtained by the jigging process offered a higher value in concentration recovery than table shaking and a specific gravity value well within the API's acceptable value (4.2 to 4.5) for drilling operations. The overall results proved the suitability of barite ore from Azara barite ore for oil drilling operations.

2.3. Magnetic separation

The magnetic separation method takes advantage of the differences in magnetic properties to separate iron-bearing minerals within the ore from the barite.

Parsonage use of magnetic separation experimentation on barite/calcite ore showed that barite had a magnetic recovery of 8.6%, as well as a non-magnetic recovery of 91.4%, for a particle size of -150 +75 microns, using sodium oleate, (Na_2SO_4), a pH value of 9, and sodium perchlorate ($NaClO_4$) [24].

Shaikh *et al.* developed a novel concept that converts non-magnetic materials into magnetic materials using magnetic surfactants, such as manganese stearate and manganese oleate [25]. The study was applied to separate a calcite/barite mixture. The presence of manganese stearate and manganese oleate increased the magnetic properties of the calcite and barite mixture, thereby making it relatively easy to disassociate the magnetic minerals from the non-magnetic mineral and thus recover calcite and barite.

Jakabsky *et al.* used magnetic separation on siderite concentrate to obtain a magnetic product, followed by flotation of a non-magnetic product to obtain a concentrate (barite) and tailings (quartz) [26]. Microscopic analysis revealed that 95-100% of barite, siderite, quartz, and slates were liberated at a particle size of 0.5 mm. Recovery of $BaSO_4$ was reported at 8.68, 91.32, 82.34 and 17.66% for magnetic, non-magnetic, barite concentrate, and quartz tailings, respectively.

2.4. Electrostatic separation

Electrostatic separation is a processing method that exploits the differences in conductivity between different minerals to separate various minerals within the ore.

Conover *et al.* used an electrostatic separation technique to separate barite and sphalerite from ordinary water concentration [27]. Wyman applied electrostatic separation to separate the barite from quartz, achieving a concentrate of 84.1% $BaSO_4$ [28].

Bittner *et al.* reported that the electrostatic separation technology has been used as far back as 1995 in Europe for the separation of conducting minerals from non-conduction minerals such as glassy aluminosilicates/ carbon, calcite/ quartz, talc/magnesite, and barite/quartz [29]. They also stated that triboelectrostatic belt separation is more cost-effective than the conventional flotation technique for barite/ quartz separation.

Furthermore, Bittner *et al.* carried out a cost study comparing the tribo-electrostatic belt separation process to conventional froth flotation for barite processing [30]. The study showed that the total capital cost for the dry tribo-electrostatic belt separation process was 63.2% of the flotation process. The total operating cost for tribo-electrostatic belt separation was 75.8% of the operating cost for flotation. Consequently, it concluded that the dry tribo-electrostatic belt separation process offers obvious advantages over floatation in reducing capital, operating, and operational costs by over 30%.

2.5. Desliming

Desliming is a unit operation often carried out on solid minerals to eliminate slime, which usually appears after milling the ores.

Ahmed postulated that a pre-request process to eliminate slimes is necessary for successful flotation as the removal of such slimes decrease reagent consumption and improve metal recovery in flotation [31].

Rabatho *et al.* described desliming as a common procedure performed in mineral processing (such as barite processing), primarily to eliminate fine particles (slime particles) that consume excessive amounts of the collector due to their large surface areas and that the coating of valuable minerals hinders the bubble-mineral contact [32].

Tingting *et al.* reported that large quantities of fine gangue minerals are generated during processing ores, such as barite, possibly due to the ore's fine grind or clayey nature [33]. Taner and Onen [34] also emphasized the need to eliminate slimes before flotation due to their detrimental effects on flotation efficiency [34].

Yu *et al.* agreed with Taner and Onen that desliming can only work when the slime fraction does not contain a high concentration of value minerals [35]. The researchers also stated that slimes increase reagent consumption and pulp viscosity and are liable to entrain into the froth product. However, Yu *et al.* admitted the uncertainty of the effect of slime removal on improved flotation performance [35].

3. Physicochemical operation

3.1. Froth flotation

Froth flotation is a highly versatile method for the physiochemical separation of particles based on differences in the ability of air bubbles to selectively adhere to specific mineral surfaces in a mineral/water slurry. Fig. 2 shows a schematic diagram of a froth flotation cell.

Estefan achieved effective selectivity between float and non-float minerals at a pH of 10 from the flotation of synthetic ores of barite and celestite [36].

Martinez *et al.* discovered that concentrate ores, which contain 93.85% barite with a recovery rate of more than 80%, can be obtained by froth floatation with minerals containing 16% barite with a high concentration of Na_2SiO_3 and a small quantity of anion sulfonated butyramide (A845) as the collector [37].

Bolin's research on barite flotation applied sulphonate and alkyl sulphate reagents [38]. The findings showed that adding alkyl sulphate reagent resulted in the fast, efficient flotation of barite particles, further resulting in a concentration grade of more than 95% $BaSO_4$. However, sulphonate reagents gave a concentration below 80% $BaSO_4$.

Houot *et al.* carried out barite flotation with sulphonate as collectors [39]. Pure barite was obtained at a pH value of 9. Results also indicated that the quality of water was a vital parameter in the flotation process. Marinakis and Shergold

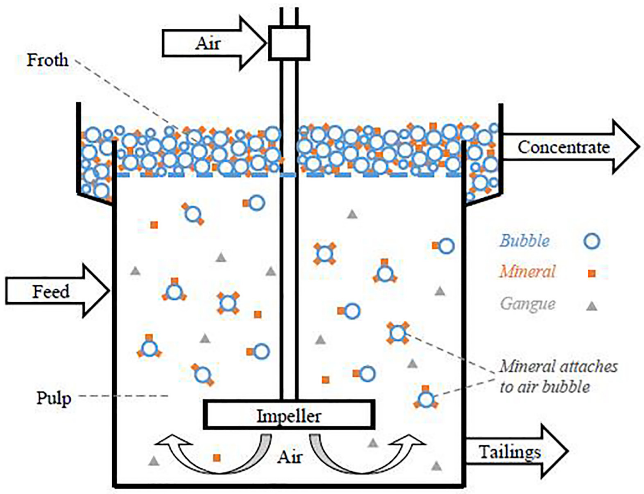

Fig. 2. A schematic diagram of a froth flotation cell.

conducted a study on the adsorption of sodium silicate by calcite, fluorite, and barite and the effect that this adsorption has on the flotation of these minerals with oleic acid [40]. The results show sodium silicate depresses these minerals by preventing oleate species from reacting with surface sites. This effect is independent of the total silica concentration.

De Cuyper and Broekaert developed an effective flowsheet for the production of barite for use in the formulation of oil well drilling mud [41]. Slaczke applied ultrasonic pre-treatment to increase the selectivity of barite by increasing the flotation rate of barite and to decrease the selectivity of fluorite by decreasing its flotation rate [42].

Ciccu *et al.* optimised a processing plant for upgrading different raw barite types to commercially acceptable standards/specifications [43]. The objective of the plant was to maximize profit for each ore type fed to the plant. The plant, located within a mineral mining complex in Sardinia, west of the Italian Peninsula, was made up primarily of two unit operations: jigging and flotation. These unit operations were comprised of a multi-stage jigging plant section integrated into the flotation section in the plant. The process, which was studied using an appropriate model, employed both primary and secondary data in the form of field and experimental data, respectively. These data were borne out of the feedstock characteristics and the machinery performance data. Data processing was done automatically using computers to obtain the optimum setting for each section of the plant to maximize profit. Results showed that the process successfully upgraded the ore to marketable standards. By taking into consideration that not all of the individual ore types are commercially viable, blending the various barite concentrates was equally studied and shown to be effective in increasing the profit by 500 Italian Lire per tonne of barite ore while considering the handling cost.

Harris applied Aero 845 and Sodium silicate as collector and depressant, respectively, and at a pH of 9 to obtain a barite concentration grade of 65.9% [44]. Meker *et al.* succeeded in using sodium alkyl sulphonate as a collector and lignite sulphonate as a depressant for barite flotation from complex ores containing barite, fluorite, quartz, bastnaesite, and oxides [45]. Sadowski achieved proper selectivity of barite by combining sodium dodecyl sulfate and sodium lignin sulfonate in a calcite-barite ore [46].

Hernáinz. and Calero discovered that due to the similarity in the physiochemical properties of barite ore and calcite, conventional collectors such as fatty acids and its derivatives were ineffective in separating barite from calcite using conventional depressants such as quebracho, organic colloids, hydrosols, and sodium phosphates [47].

Hadjiev *et al.* carried out the flotation of barites from a complex iron ore deposit in Kremikovtzi, Bulgaria, to produce high-grade barite concentrate from complex iron ores [48]. Barite flotation was performed using collecting agents OMC 199 and AERO 8-15 in the ratio of 2:1 at a total dosage rate of 400-450 $g.t^{-1}$, and water glass was used as the silica depressant at the application rate of 4-4.5 $kg.t^{-1}$, while OrePrep F 501 consumption at 10-15 $g.t^{-1}$ served as the frother. The quality of the barite obtained met OCMA (Oil Companies Material Association) and API (American Petroleum Institute) standards for oil and gas operations.

Sonmez and Cebeci used oil agglomeration to recover barite particles [49]. Operating parameters such as pH, stirring speed, quantity of the collector (Na-Oleate), quantity of bridging liquid (kerosene), suspension conditioning time, collector stirring time, agglomeration time, and solid concentration were studied to determine their optimum conditions for the highest quantity of barite recovery using oil agglomeration. Examination of the experimental results gave the optimum oil agglomeration conditions of barite as follows: pH: 10, stirring speed: 1500 rpm, quantity of Na-Oleate: 3 $kg.t^{-1}$, quantity of kerosene: 80 $L.t^{-1}$, suspension conditioning time: 2 min, collector stirring time: 1 min: agglomeration time: 2 min and solid concentration: 5 wt%.

Pradip and Rai carried out a flotation experiment of bastnaesite from calcite and barite, observing that hydroxamate collectors had a higher selectivity than the conventional fatty acid (oleate) [50]. It was further observed that bastnaesite responded to hydroxamate flotation more strongly than both barite and calcite.

Ulusoy and Yekeler's work on barite's floatability showed that different grinding devices affected its (barite) surface properties differently [51]. The more elongated and smoother the barite particles with lower degrees of wettability values indicate more hydrophobicity, independent from the mill type. Meanwhile, particles with rounder and rougher surfaces lead to higher wettability or less hydrophobicity.

Gurpinar studied the effects of ultrasonic waves on the flotation of calcite, barite, and quartz in single and mixed minerals [52]. For single minerals, ultrasonic treatment has a positive effect on the flotation performance of calcite and barite, but a negative effect is shown in the case of quartz. Similar results were obtained in the case of mixed minerals. This was attributed to the difference between collector adsorption mechanisms, characterised by infrared spectroscopy. Furthermore, while chemical adsorption takes place on calcite and barite, physical adsorption occurs in quartz.

Raju *et al.* used Oleic acid (800 $g.t^{-1}$) as the collector and Sodium silicate (2000 $g.t^{-1}$) as a depressant at a pH value of 9 to obtain a high barite concentration grade of 93.24% $BaSO_4$ [53].

Singh *et al.'s* work on adopting a flotation process on barite ore resulted in the barite recovery of over 88%, with a specific gravity of 4.25 [54]. The results of the bench-scale studies were validated through large-scale trials. Based on the results of this study, a process flowsheet was developed to process the barite waste dump sample.

Lu affirmed that Ferric cation (Fe^{3+}) can heighten the floatability of barite using sodium oleate as a collector and that Fe^{3+} activates the barite through the generation of hydroxylated complex or hydroxide sediments on the barite [55].

Achusim-Udenko *et al.* obtained a significant upgrade in barite concentrate, from 75.4% to 91.9% in the flotation recovery of Azara barite (Nassawara State), using locally processed palm bunch palmitic acid from burnt empty palm (Eleasis guineesis) acting as collector, and sodium silicate as a depressant [56]. However, the experiment also recorded a high material loss of 5.5–8.1%.

Huang *et al.*'s research indicates that morphological properties and shape of barite particles can affect their flotation results [15]. Zhao *et al.* used Sodium Oleate (700 $g.t^{-1}$) as the collector and water glass (500 $g.t^{-1}$) as a depressant at a pH value of 8 to obtain a high barite concentration grade of 98.21% $BaSO_4$ and a recovery of 80.71%. [57]

Wang *et al.* conducted a flotation test on low-grade barite ore from Myanmar, assaying 64.32% $BaSO_4$ with the use of 800 $g.t^{-1}$ sodium oleate and 500 $g.t^{-1}$ of sodium silicate as collector and depressant, respectively [58]. The flotation test was performed at a pH value of 8. The effects of grinding fineness, type, and dosage of flotation reagent were further investigated. Findings showed that optimum conditions, a grinding fineness of -200 meshes and an assays value of 64.32% (using a two-stage flotation roughing system), resulted in acceptable barite concentrates of 96.32% and 91.26% $BaSO_4$ at recoveries of 91.94% and 5.25%, respectively.

Wang *et al.* performed a flotation test using oxidized paraffin soap as the collector and sodium silicate as the gangue mineral inhibitors and obtained an acceptable barite concentration of over 95% $BaSO_4$ and a recovery of 96% [19]. Kecir and Kecir used Petronate L (1000 $g.t^{-1}$) as the collector, in the absence of a depressant, and at a pH value of 6.5 to obtain a barite concentration grade of 93.4% $BaSO_4$ and a recovery of 87.4%. [59]

Bulatovic pointed out that barite flotation can be carried out by either reverse or direct flotation [60]. Removing base metals sulfides or pyrite leaves a concentrated barite in the tailings, which is then recovered by flotation and is referred to as reverse flotation. The flotation of barite from the ores containing fluorspar, silicates, and rare earth oxides (REO) is called direct flotation.

Shekiladze *et al.* obtained barite concentrates of 92.11% and a recovery of 81.85% from the beneficiation of silver-barite ore by flotation, thus indicating that the barite ore concentrate satisfies the chemical and industry demands in terms of quality and specification [61].

Demeekul *et al.*'s research on flotation operating parameters revealed that the immersion depth of the downcomer and air flow rate (in a flotation column) influence the performance of barite/associated minerals separation [62]. At an air flow rate of 20, 30, and 40 $L.min^{-1}$, the barite concentrate is nearly constant at about 70% $BaSO_4$. However, it increases at a depth of 15 m. The optimum air flow rate of 30 $L.min^{-1}$ gives a barite concentration grade of 85% $BaSO_4$ with recovery and enrichment figures of 73% and 1.3, respectively.

Raju *et al.* studied the processing of low-grade barite dumps interlocked with schist and slate gangue using amine as a collector (reverse flotation) to avoid the collector coating on the barite sample [63]. Instead of conventional flotation cells, a flotation column was applied due to its inherent advantages. Results indicated that a barite concentrate assaying 95% $BaSO_4$ could be obtained with a recovery of around 70% in a single-stage column flotation. The recovery was improved to 85% by incorporating scavenging flotation using conventional cells. Based on the laboratory results, a commercial flotation column with the capacity of treating 700 tpd was designed and commissioned.

Raju *et al.* successfully applied a reverse flotation technique in the laboratory and commercially based flotation of mangampet barite using Armoflote-17, Liquid B-50, and Sokem-524C (a vegetable oil-based amine collector) in a flotation column, increasing the barite assay from 82% to 94–97% [63]. Results also showed that nearly 50% of the barite was lost in the tailings due to the ineffectiveness depression of barite by starch.

Ren *et al.* selectively separated fluorite, barite, and calcite by flotation, using valonea extract and sodium fluosilicate as depressants and sodium oleate as the collector [64]. The flotation result revealed that while 94% of the calcite was effectively depressed using the valonea extract, a fluorite recovery of 95% was achieved in the follow-up flotation process using sodium fluosilicate to depress the barite.

Chen *et al.* applied modified starch to selectively separate barium from fluorite [65]. Results indicate that at values of 13.16×10^{-5} mol/dm3 of sodium oleate and 250 $mg.dm^{-3}$ of modified starch (in a solution with a pH of 7), a high level of selective separation was achieved between barite and fluorite. Analysis of the Fourier transform infrared spectroscopy results revealed that both the fluorite and barite surfaces can be adsorbed by the modified starch. Further analysis using zeta potential (ZP) shows that the modified starch had an insignificant effect on sodium oleate. adsorption on the fluorite surface. However, there was some degree of interference on the barite surface (by the modified starch sodium on sodium oleate adsorption).

Chen *et al.* carried out flotation studies of fluorite and barite with sodium petroleum sulfonate (SPS) as the collector and sodium hexametaphosphate (SHMP) as the depressant [65]. Examination of the flotation results revealed that SPS was very effective within a pH value ranging from 7 to11, even at a low temperature (5 ^oC). The floatability of fluorite and barite were just about the same. At a pH value of 11, the depressant SHMP depressed fluorite (as expected) rather than barite and showed excellent selective inhibition of fluorite.

Results from Fourier-transform infrared spectra and zeta potential showed that SPS is capable of being adsorbed on fluorite and barite surfaces, and SHMP had little effect on the adsorption of SPS on a barite surface, although it interfered with the adsorption of SPS on a fluorite surface through strong adsorption.

Chen *et al.* carried out floatation separation of barite from calcite by using sodium dodecyl sulfate (SDS) as the collector and sodium silicate (SS) as the depressant [66]. Results revealed that SDS has a high collecting ability for both calcite and barite and that the flotation separation of barite from calcite cannot be achieved using only SDS. The selective depression effect of SS on calcite occurred by controlling the pulp pH at 9.0 in the presence of SDS, leading to a product with 95.54% $BaSO_4$ concentrate and a recovery of 86.11% from the unprocessed ore.

Chen *et al.* conducted a laboratory-based flotation of pure artificially mixed fluorite and Chongqing barite using NaOL, modified starch, HCl, and NaOH [66]. Results indicated an increased barite recovery from 89.62 to 91.16% using NaOL.

Denga *et al.* proved that acidified water glass (AWG) is an effective depressant in separating barite from calcite using NaOl as the anionic collector [67]. Zeta potential measurements showed that AWG inhibited the adsorption of NaOL onto the barite surface but did not hinder the interactions between NaOL and the calcite surface. The adsorption of silicic acid dimer onto the calcite surface resulted in the selective depression of calcite due to the positively charged surface of calcite. In summary, this research established AWG as an efficient and effective depressant for the selective separation of barite from calcite using the established anionic collector NaOL. Fig. 2 gives the schematic diagram for the flotation separation of barite from calcite with depressant AWG and collector NaOL.

Lu *et al.* utilised lauryl phosphate as a collector for barite flotation [68]. Results from microflotation, contact angle, and zeta potential indicate that lauryl phosphate is adsorbed on the barite surface and, thus, achieves superior flotation efficiency in a wide pH range. The interfacial water structure and wetting characteristics of the barite surface with/without lauryl phosphate adsorption were also evaluated by molecular dynamics simulations (MDS). The results from molecular dynamics simulations and interaction energy calculations align with the experimental results, which suggest that lauryl phosphate might be a potential collector for the flotation of barite.

Liu *et al.* also utilized citric acid as a depressant for fluorite, attaining a high success in the flotation separation of fluorite from barite [69]. Microflotation study revealed that using sodium oleate (NaOL) as the collector showed effective floatability of fluorite and barite. However, when using citric acid as the depressant, fluorite alone was selectively depressed. Adsorption and adsorption experiments and inductively coupled plasma atomic emission spectroscopy analysis showed that the addition of citric acid had no major consequence on the Ba^{2+} ion on the barite surface, unlike in the case of fluorite, where citric acid resulted in the dissolution of Ca^{2+} from the fluorite surface. Lastly, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), zeta potential (ZP) measurements, and solution chemistry computations further indicated that the selective inhibition of fluorite by citric acid could be a result of the dissolution of the calcium cation (Ca^{2+}) from the mineral surface, which lowers the total sum of activated sites for NaOl adsorption.

Oyolola *et al.* applied an indirect flotation technique (at varied feed sizes and pH values) to purify barite from Kiana (Alaska, United States) for the purpose of utilizing it in the formulation of drilling mud for use in the oil and exploration field [70]. Corn starch, corn oil, and oleic acid were used as the flotation reagents. An optimum concentrate assay of 72.96% BaO and a specific gravity of 5 were obtained at a feed particle size and pH value of 300 mm and 7, respectively. These results show that Kiana barite offers an excellent prospect for oil and gas drilling operations.

Xiong *et al.* applied salicylhydroxamic acid (SHA) as a collector in the flotation of astnaesite, barite, and calcite [71]. The experiment studied the flotation responses of astnaesite, barite, and calcite using salicylhydroxamic acid (SHA) as the collector in micro-flotation experiments. Fourier transform infrared (FT-IR) analyses, X-ray photoelectron spectroscopy (XPS), solution chemistry analyses, and zeta-potential measurements were carried out on these samples. In terms of micro-flotation of the barite, results revealed that the barite has an insignificant flotation response. The results of FT-IR, XPS, and zeta-potential measurements showed that only physical adsorption of SHA occurs on the surface of the barite, as opposed to bastnaesite, which experienced both physical and chemical adsorption of SHA.

Liu *et al.*'s research on the effect of barite particle size (in the form of slime) on fluorite flotation revealed that while gelatinized starch was efficient in the selective depression of the barite flotation with various size fractions, the flotation of fluorite using sodium oleate (as the collector) was insignificance [69]. These results indicate adequate separation of fluorite from barite using a combination of galvanized starch/sodium oleate. However, fine barite particles within a mixture of various mineral particles interfere with the fluorite flotation considerably. Further tests involving Zeta potential measurements, light microscope observations, and turbidity uncovered the hetero-coagulation between fluorite and barite slimes, resulting in slime coating of barite onto the fluorite surface. Gelatinized starch was unable to entirely eliminate the harmful effects of the barite slime coating due to the fluorite-barite mass entrainment.

Afolayan *et al.* noted that environmental concerns posed by flotation, adhering chemicals, and elimination of water-soluble salts of Na, K, Ma, and Ca in barite due to acidic leaching were not considered in previous studies [72].

Deniz *et al.* investigated the effect of pH, flotation time, collector dosage, and depressant dosage on rougher flotation of the barite tailings (containing a $BaSO_4$ concentration of 37%) [73]. They used two mathematical models, artificial neural network (ANN) and multivariable linear regression (MLR), to compare its recovery and grade for subsequent rougher flotation optimization. The coefficient of determination (or the concentrate recovery) and the concentration grade for both models were given as 0.828/0.995 and 0.977/0.960, respectively. Results showed that the ANN model offered better results than the MLR model in the recovery of the rougher concentrate.

4. Chemical separation operations

4.1. Leaching

Leaching uses acidic or alkaline reagents to eliminate the metal oxides and other insoluble impurities attached to barite, resulting in its (barite) separation from them.

Andrews and Collings reported that a few bleaching studies were conducted on high-grade barite concentrates to remove iron staining [16].

Khan *et al.* applied a range of HCl concentrations ranging from 5% to 30% at ambient temperature and identical time intervals to enhance the quality of barite from Gunga (Pakistan) deposits to internationally required standards/specifications for use in a host of chemical industries such as paint, rubber, filler, plastic, etc., industries [74].

Khan *et al.* produced a global standard/specification barite (for industrial use) using a thirteen-minute chemical treatment process on a barite sample from Pakistan's Hazara area [75].

Essalhi *et al.* published a paper titled “Evidence of a high-quality barite in Drâa-Tafilalet region, Morocco: a non-upgraded potential” [2]. In this paper, a flow sheet was developed for a proposed chemical treatment of barite using an acid treatment. The flowsheet was built on physical separation processes: manual sorting, crushing, screening, washing, gravity, and magnetic enrichment.

5. Combination of processing techniques

Ciccu *et al.* upgraded a barite pre-concentrate of 85.5% $BaSO_4$ with a grade of 43.75% by grinding, magnetic separation, and shaking table concentration [43]. A new barite concentrate of 91.92% $BaSO_4$ grade with 41.74% $BaSO_4$ and 41.74% recovery was achieved.

Ibisi investigated the mineralogical composition and thermal behaviour of a barite sample from Nigeria [76]. Using a combination of magnetic separation and flotation (with Na-cetyl sulphate as a collector at a pH of 10.8), a $BaSO_4$ concentrate of 96.8wt% was achieved.

Ozbas and Hicyilmaz experimented on barite and fluorite minerals from Eskisehir-Beylikahir, Turkey, using gravity concentration, froth flotation, and high-density magnetic separation operations to recover barite and fluorite [77]. A combination of gravity concentration-flotation-magnetic separation (in that order) offered the optimum results, a barite concentration assaying 87.45% $BaSO_4$ and a barite recovery of 49.61%. In the flotation process, the collector and depressant were 900 $g.t^{-1}$ S3903 and 1250 $g.t^{-1}$ Na_2SiF_6, respectively.

Onyemobi and Nwoko processed Azara barite ore using a combination of jigging and magnetic separation processes [78]. Results showed that the processed barite met the required standard/specifications for oil and gas operations and several other chemical industrial needs. Additionally, a comparison between the applied jigging and magnetic separation processes showed that the latter produced a less satisfactory result than the former.

Hadjiev *et al.* studied the production of a high-grade barite concentrate from complex iron ores containing limonite, hematite, and siderite [48]. High-intensity electromagnetic wet separation and flotation beneficiation were employed. The collecting flotation agents OMC 199 and AERO 8-15 (2:1 ratio) were applied at the total dosage rate of 400 - 450 $g.t^{-1}$. Water glass was used as a silica depressant at the application rate of 4 - 4.5 $kg.t^{-1}$. Results showed a high-grade barite concentrate assaying 97-98wt. %.

Oladapo and Adeoye-Oladapo used a combination of gravity and electromagnetic methods to characterised barite in vein deposits in the Tunga area of northwestern Nigeria [79]. The study revealed a barite average specific gravities of 3.16 and 4.24, while the host sandstone rock recorded a specific gravity of 2.63.

Grigorova *et al.* reported the Kremikovtzi deposit as a complex ore comprising iron as the valuable minerals and barite, lead, and manganese as the gangue minerals [80]. Characterization results indicated that barite could be recovered from tailings using the flotation method preceding magnetic separation.

Bhatti *et al.* processed barite ore from the Duddar Area, Pakistan, using flotation and leaching processes and obtained a barite concentrate of 98.86% from an ore containing 76.04% $BaSO_4$ [5]. The final barite concentrate conformed to the specifications of industrial-grade barite.

Nzeh *et al.* investigated the use of two forms of gravity separation techniques, jigging and shaking tabling techniques, and a chemical process in the form of acidic leaching (using HCl and H_2SO_4 acids) to process raw Azara barite ore from Nasarawa State, Nigeria [21]. The efficacy of the processing technique was measured in terms of the value of the specific gravity in meeting the global standard of 4.20 to 4.50 for oil and gas exploration. The result showed that the use of jigging and shaking tabling techniques, along with a leaching treatment using 1.0 molar concentration of HCl and H_2SO_4, gave the maximum value range in specific gravity in a range of 4.39 to 4.46, up from a raw value of 3.85. Consequently, the results of this research confirmed that the use of jigging, shaking tabling, and acidic leaching can upgrade Azara barite to meet the requirement for use in oil and gas drilling.

Deniz and Guler applied dry/wet high gradient magnetic separation (HGMS) and bleaching methods to investigate the rejection rate of coloring impurities from barite ore [81]. This study was carried out to increase the brightness index of the barite concentration. Results showed a substantial enhancement in the product quality using sulfuric acid leaching at a 10% acid concentration for 30 minutes. However, colouring impurities could not be adequately eliminated to obtain a marketable product. However, by applying bleaching at 15% HCl concentration for 15 minutes, a barite of marketable properties was obtained. Beneficiation studies revealed that by using wet HGMS followed by HCl bleaching, the brightness index of barite could be increased from 68.05% to 90.12%.

Mgbemere *et al.* studied the jigging, froth flotation, and chemical leaching of +180 µm, (−180 + 90) μm Azara barite, using pine oil, oleic acid, HCl, and HOCl [82]. Leaching was introduced because an initial study that was carried out indicated (through the chemical analysis) that after froth flotation, the amount of silica present in barite was still very high. Results showed an increase in the specific gravity of Azara barite ore from an initial value of 3.27 ± 0.03 to 4.38 and a $BaSO_4$ concentration increase from 64.6% to 99.5%. Research findings further indicate the need to eliminate water-soluble Ca, Mg, Na, and K salts to aid the rheology of drilling fluid and filtration control in drilling applications.

Mgbemere *et al.* conducted a laboratory-based jigging and froth flotation of (−350 + 180) µm size Azara barite using NaOH and oleic acid [83]. Results indicate an increased barite specific gravity from 3.72 to 4.23 at a 92.9% recovery at a pH of 7, while the pH at 3 gave the lowest specific gravity value of 3.78.

Philips and Paul used a combination of jigging, froth flotation, and acidic leaching to improve Akpet 1 barite specifications for use in oil drilling operations [84]. For flotation, pine oil, oleic acid, and HCl were used as reagents, while 0.2 M of HCl was used in the acidic leaching. After acidic leaching, the percentage of the barite in the $BaSO_4$ increased from an (initial) unprocessed value of 62.101% to 91.212%. In addition, the specific gravity rose from an unacceptable initial API value of 3.03 to an acceptable API value of 4.39 after processing. The Mohr's hardness scale and pH value were recorded as 3 - 25 and 6.8, respectively. These results show that Akpet 1 barite can be processed to meet the specifications for use in the formulation of drilling fluid for oil and gas operations.

Popoola and Fadayini built on Deniz *et al.'s* [73] experimentation on the use of mathematical models in the recovery and grade for subsequent rougher flotation optimization [85]. Using the response surface methodology, they optimized low-grade barite from Azara, in Nassarawa state, Nigeria, using a batch experimental design. The experimental design was conducted using the box-Behnken Design (BBD) and the central composite design (CCD) approaches. The results were compared with those obtained using an artificial neural network (ANN). Their respective mean squared error value, regression coefficient value, and absolute average deviation for the BBD, CCD, and ANN showed that ANN is the most suitable model.

Boamah evaluated the economic viability of processed barite production in three African countries: Nigeria, Morocco, and Algeria [86]. An economic model consisting of a constant dollar and after-tax discounted cash flow was used to evaluate the feasibility of processed commercial local barite production in the three countries. Results showed that Nigerian and Algerian processed barite production was short of the required level demanded by their oil and gas (IOC's) industry and export. Morocco, however, exceeded the quantity of processed barite production required for export.

3. Conclusion

Barite ($BaSO_4$) is an important industrial mineral that can be used in various applications based on its physical and chemical properties. It is used mainly by the oil and gas industry as a weighting agent for drilling operations. This paper has reviewed the various technologies used in processing barites for various applications. The reviewed techniques show that gravity separation and froth flotation are the two most widely used methods for barite processing.

As encountered in the course of the survey, the advantages of froth flotation over gravity separation methods include:

- Broad application

Since the gravity separation technique's effectiveness is based on the nature of the barite ore, while the froth flotation technique is based primarily on the flotation reagents applied for separation. The Froth flotation technique can thus be used regardless of the nature of the barite ore.

- Greater separation efficiency

Froth flotation is very efficient when the barite separation involves fine minerals, unlike gravity separation, which is tailored to barites of coarse sizes. Furthermore, issues such as difficulty in the recovery of barite from its unwanted associate mineral in the form of fine grains complexes are easily solved by froth flotation.

The drawbacks of the use of froth flotation that render gravitation separation of greater benefit than the froth flotation technique are:

- Cost-effectiveness

Gravity separation is a relatively simple, cost-effective, and uncomplicated method. Meanwhile, froth flotation involves complex equipment and often results in excessive consumption of reagents and energy. This results in an increase in the overall operational cost.

- Environmental concerns

Since gravity separation techniques do not entail using chemicals or water (in the form of reagents), deleterious effects on the environment are insignificant or very limited. Thus, gravitational separation techniques can be said to be an environmentally friendly process. The same cannot be said of froth flotation, which involves applying various chemicals, often raising environmental concerns.

- Number of factors considered

Unlike gravity separation, which involves fewer factors, the use of froth flotation involves quite a number of factors that can ultimately distort the final outcome. These critical factors include pulp pH, pulp concentration, pulp temperature, agitation/flotation time, grinding fineness, flotation reagent system, aeration, agitation, flotation time, and water quality.

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