BENEFICIATION AND ASSESSMENT OF AZARA BARITE ORE FOR DRILLING FLUID IN OIL AND GAS INDUSTRY

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ABSTRACT

In this research work, raw barite ore as one of the component of drilling fluid was successfully beneficiated using froth flotation and purification method to assess its suitability in oil and gas industry. The barite ore was source from Azara, Awe local Government of Nasarawa State, Nigeria. Chemical analysis on the raw barite ore indicates that it contains 56.224% of barium component and 15.247% Sulphur oxide with a specific gravity value of 3.787±0.03. After beneficiation and purification operation, the specific gravity value of the barite has increased to 4.166±0.029 while the barium and sulphur increased to 82.116% and 9.061% respectively. With purification, the specific gravity values of Azara barite obtained were 3.95, 4.166 and 4.05 corresponding to pH values of 5, 7 and 9 respectively. Frothed barite with pH of 7 was purified with 0.2M HCl and a mixture of 0.2M HCl and HOCl. The X-ray diffraction patterns show that highly crystalline peaks were obtained after froth flotation while more phases are added with purification. Therefore, since the XRD pattern peaks of barite mined from Azara are in agreement with the peaks of imported barite, XRF data and SEM images are in line with the imported barite for drilling fluid application, then Azara barite ore has the potential to replace imported barite in Nigeria when given required attention.

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LIST OF ABBREVIATIONS

API	American Petroleum Institute
BSE	Back-Scattered Electrons
CL	Catghodoluminescence
FEG	Field Emission Guns
ISO	International Organisation for Standardisation
LTOBM	Low Toxicity Oil Based Mud
LWD	Logging While Drilling
MWD	Measurement While Drilling
OB	Oil Base
OCMA	Oil Companies Materials Association
OBM	Oil Based Mud
PAX	Potassium Amyl Xanthate

PAC	Polyanionic Cellulose
PIBX	Potassium Isobutyl Xanthate
PEH	Petroleum Engineering Handbook
ROP	Rate of Percentage
RMRDC	Raw Material Research and Development Council
SBM	Synthetic Based Mud
SE	Secondary Electron
SEI	Secondary Electrons Image
SIBX	Sodium Isobutyl Xanthate
SEM	Scanning Electron Microscopy
SEX	Sodium Ethyl Xanthate
SIPX	Sodium Isopropyl Xanthate
WB	Water Based
WBM	Water Based Mud
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

CHAPTER ONE

1.0 INTRODUCTION

Barite ($BaSO_4$), a name that was derived from the Greek word “barus” (heavy), is the mineralogical name for barium sulphate. In commerce, the mineral is sometimes referred to as “barites.” As used in this report, the term “primary barite” refers to the first marketable product, which includes crude barite (run of mine) and the products of simple beneficiation methods, such as washing, jigging, heavy media separation, tabling, flotation, and magnetic separation (Tanko *et al.,* 2015). Most crude barite requires some upgrading to minimum purity or density. Barite that is used as an aggregate in a “heavy” cement is crushed and screened to a uniform size. Most barite is ground to a small uniform size before it is used as filler or extender, an addition to industrial products, or a weighting agent in petroleum well-drilling mud (American Petroleum Institute (*API*) or Oil Companies’ Materials Association *OCMA*) specification of barite (Cheraghian *et al.,* 2018).

Barite used for drilling petroleum wells can be blue, black, buff, brown, or grey depending on the ore body. It must be finely ground so that at least 97.0% of the material, by weight, can pass through a 200-mesh (75-micrometer) (Tyler) screen, and no more than 30.0%, by weight, can be less than 6 micrometres, effective diameter, which is measured using sedimentation techniques. The ground barite also must be dense enough that its specific gravity is 4.2 or greater, soft enough to not damage the bearings of a tricone drill bit, and both chemically inert and containing no more than 250 mg/kg of soluble alkaline salts. A small percentage of iron oxide (FeO) is allowable (Nzeh *et al*., 2017). An additional feature of barite is non-interference with magnetic measurements taken in the borehole, either during logging-while-drilling or in separate drill-hole logging. In offshore drilling, the U.S. Environmental Protection Agency limits the content of mercury to 1 milligram per kilogram of barite and that of cadmium to 3 mg/kg of barite. Although barite ($BaSO_4$)

contains a heavy metal (barium), it is not a toxic chemical under section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 because it is very insoluble in water (Tanko *et, al.,* 2015).

Several industrial non-metallic minerals have been reported to be available in Nigeria but have either been left unexploited or have experienced very little exploitation. One of such minerals is barite, a very important industrial raw material used as a pigment for making paints, in paper coating applications and more importantly as a weighting ingredient in drilling for crude oil (Tanko *et al.,* 2015).

Due to its high specific gravity value (4.5), barite helps to counteract pressure formation during drilling thereby giving the drilling bit the necessary density required. Other materials used as weighting agents include celestite, calcium carbonate, Ilmenite and synthetic haematite. As the number of oil rigs around the world increases, the demand for barite will also greatly continue to increase. Barite is usually the starting point in the manufacture of other compounds of barium (Strbac *et al.,* 2006).

One of the major export commodity for Nigeria is crude oil which is obtained from the hydrocarbon bearing regions of the country. A very important ingredient used in the drilling of crude oil is barite. Most of the barites currently used are imported because the ones being processed in Nigeria have specific gravity values which are lower than the industrially accepted standard. This is mainly due to the fact that a lot of impurities are associated with the barite ores. Barite ore mined from Wuse-Azara is one of many deposits that can be found in Nigeria (Mgbemere *et al*., 2018). Through petrology and geochemical investigations, the mineralisation potentials of Wuse-Azara barite deposits have been reported with relatively high amounts of $BaSO_4$ in the veins of the middle Benue Trough (Tanko *et al.,* 2015). Several high quality barite samples have been reported in the literature to be beneficiated from low grade barite ores (Tanko *et al.,* 2015). The strategies used to beneficiate these barite ores depend on factors like the grade of the ore, nature of the gangue and their liberation size. Gravity separation which is about the oldest method to separate minerals and froth flotation are two of the most common methods used to beneficiate barite.

Using froth flotation, barite samples with concentration of over 97.0% BaSO4 have been obtained from different sources: tailings, from complex iron ore in Bulgaria 96.3% and 91.3% respectively, from low grade barite ore from Myanmar up to 88.0 % $BaSO_4$ from low grade barite in India (Cheraghian *et al.,* 2018).

Flotation of barite using (*Eleasis guineesis*), analytical grade palmitic acid as collector and sodium silicate as depressant have led to recovery of up to 91.1 % $BaSO_4$ for Nigerian barite ore (Tanko *et al.,* 2015). Modified starch has been used to remove fluorite from barite using froth flotation and the starch is believed to have acted as a depressant to barite in neutral solutions. Computational processing through operations research has also been used to model and enhance the outcome of the jigging and flotation process (Cheraghian *et al.,* 2018).

The type of crushing mill used also determines the physical characteristics of barite like shape, roughness, wettability of the barite produced and there exists a correlation between the shape and wettability characteristics of the barite. Grinding kinetics of calcite and barite minerals in terms of the specific rates of breakage, the primary breakage distribution function, also affect the shape of barite (Leaching is also another beneficiation method for barite and has been used to process complex sulphide barite ore using Ferric chloride solution at temperatures between 80 to 150 ^oC. Jigging, gravity separation and leaching has also been used to beneficiate Wuse-Azara barite ore with high specific gravity values obtained (Nzeh *et al.*, 2017).

1.2 Aim & Objectives of the Research

The aim of this research is to beneficiate Azara barite ore deposit using froth floatation method to produce high barite concentrate. The specific objectives of this work include the following;

(a). To beneficiate and purify the barite ore mined from Azara using froth floatation techniques in order to achieve highly purified $BaSO_4$.

(b). To characterize the barite ore mined from Wuse-Azara, Awe local government of Nasarawa State, Nigeria and its purified components.

(c). To compared percentage purity of barite mineral mined in Nigeria (Azara) with the imported one.

1.4 Scope of the Research

The scope of this research is limited to beneficiate Azara barite ore using froth floatation and purification with oleic acid as collector, sodium silicate as modifier and methyl isobutyl carbinol (MIBC) as frother.

1.5 Statement of the Research Problem

Barites currently in used are imported because those being processed in Nigeria have specific gravity values of 4.2 which are lower than the industrially accepted standard for drilling fluid application. Impurities are the major associate of Azara barite ores; as manufacturers of barium salts accept only high-grade concentrates with very low pollutants to be use hence, the need to beneficiate the barite ore mined from Azara to remove more impurities.

1.6 Justification of the Study

The major export commodity for Nigeria is crude oil which is obtained from the hydrocarbon bearing regions of the country. Barite is an important ingredient used in the drilling mud application. Barite ore mined from Wuse-Azara is one of many deposits that can be found in Nigeria. Through Petrology and Geochemical investigations, the mineralisation potentials of Wuse-Azara barite deposits have been reported with relatively high amounts of $BaSO_4$ in the veins of the middle Benue Trough, hence the need for the beneficiation of barite mined from Azara (Mgbemere *et al*., 2018).

Using froth flotation, barite salt with concentration of over 95.0% $BaSO_4$ have been obtained from different sources: tailings, from complex iron ore in Bulgaria 96.3% and 91.3% respectively, from low grade barite ore from Myanmar up to 88.0% $BaSO_4$ from low grade barite in India. A combination of jigging, froth flotation and leaching have been used to beneficiate Wuse-Azara barite ore. Leaching was introduced because an initial study that was carried out indicated through the chemical analysis that after the froth flotation, the amount of silica still present in barite was still very high (Markl *et al*., 2019).

Consequently, the market structure has undergone a major change compared to the previous period. This chiefly concerns the more stringent quality requirements for the different utilizations; in paint and plastic companies as filler, as a pigment for paper, textiles and paint. Attainment of these objectives resulted in the reduction of the quantity of barite imported into the country. It will be of benefit to companies whose interests are in paint manufacturing, drilling and paper making. The country will also benefit since the amount of foreign exchange spent on the imported barite will be reduced while creating employment for quite a number of unemployed people (RMRDC, 2016).

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Barite

Barium sulphate ($BaSO_4$) often occurs as large veins or beds, as gangue mineral in various mineral veins, in limestone's, sandstones and the like deposits. The ores are generally low grade and require concentration by floatation to meet market specifications (Tanko *et al.,* 2015). Barite, which has the ability to influence other materials with its basic characteristics, makes this heavy spar indispensable in maintaining the high specifications and uniform viscosity needed in all rotary drilling fluids. The barite beneficiation process is one of floatation, it is used as an ingredient in "heavy mud" for oil-well drilling, for which purpose specifications demand a material meeting the drilling "mud" specifications (Abdou *et al.,* 2018).

1. Fineness: 98.0% finished product must pass through 200 mesh; (90-95.0 %) will pass through (325 mesh screen)
2. Specific Gravity: required is 4.3 or better. This product contains 90.0% or more barite ($BaSO_4$).
3. Viscosity: Maximum viscosity allowed is 60cnp. The usual weight is 16 lbs./gal. on the mud scale.

2.1.1 Barite Occurrence

Barite often occurs as concretions and void-filling crystals in sediments and sedimentary rocks. It is especially common as concretions and vein fillings in limestone and dolostone. Where these carbonate rock units have been heavily weathered, large accumulations of barite are sometimes found at the soil-bedrock contact. Many of the commercial barite mines produce from these residual deposits (Cheraghian *et al.*, 2018).

Barite is also found as concretions in sand and sandstone. These concretions grow as barite crystallizes within the interstitial spaces between sand grains. Sometimes crystals of barite grow into interesting shapes within the sand. These structures are known as "barite roses". They can be up to several inches in length and incorporate large numbers of sand grains. Occasionally barite is so abundant in sandstone that it serves as the "cement" for the rock (Abdou *et al.*, 2018).

Barite is also a common mineral in hydrothermal veins and is a gangue mineral associated with sulfide ore veins. It is found in association with ores of antimony, cobalt, copper, lead, manganese, and silver. In a few locations barite is deposited as a sinter at hot springs.

2.1.2 **Physical properties of barite**

Barite properties is shown in Table 2.1. It is one of just a few non-metallic minerals with a specific gravity of four or higher. Combine that with its low Mohs-hardness (2.5 to 3.5) and its three directions of right-angle cleavage and the mineral can usually be reliably identified with observations (Tanko *et al.*, 2015).

Table 2.1: Physical properties of barite

Physical Properties	Appearance
Chemical Classification	Sulphate
Colour	Colourless, white, light blue, light yellow, light red, light green
Streak	White
Luster	Vitreous to pearly
Diaphaneity	Transparent to translucent
Cleavage	Very good, basal, prismatic
Mohs Hardness	2.5 to 3.5
Specific Gravity	4.2 to 4.5
Diagnostic Properties	High specific gravity, three cleavage directions at right angles
Chemical Composition	Barium sulphate, BaSO4
Crystal System	Orthorhombic
Uses	Drilling mud; high-density filler for paper, rubber, plastics

2.1.3 Uses of Barite

Most barite produced is used as a weighting agent in drilling muds. This is what 99.0% of the barite consumed in the United States is used for (Abdou *et al.,* 2018). These high-density muds are pumped down the drill stem, exit through the cutting bit and return to the surface between the drill stem and the wall of the well. This flow of fluid does two things:

i. It cools the drill bit; and
ii. The high-density barite mud suspends the rock cuttings produced by the drill and carries them up to the surface (Tanko *et al.,* 2015).

Barite is also used as a pigment in paints and as weighted filler for paper, cloth and rubber. The paper used to make some playing cards has barite packed between the paper fibers. This gives the paper a very high density that allows the cards to be "dealt" easily to players around a card table. Barite is used as weighting filler in rubber to make "anti-sail" mud flaps for trucks (Mgbemere *et al*., 2018).

Barite is the primary ore of barium, which is used to make a wide variety of barium compounds. Some of these are used for x-ray shielding. Barite has the ability to block x-ray and gamma-ray emissions. Barite is used to make high-density concrete to block x-ray emissions in hospitals, power plants, and laboratories (Abdou *et al.,* 2018).

Barite compounds are also used in diagnostic medical tests. If a patient drinks a small cup of liquid that contains a barium powder in a milkshake consistency, the liquid will coat the patient's oesophagus. An x-ray of the throat taken immediately after the "barium swallow" will image the soft tissue of the oesophagus (which is usually transparent to X-rays) because the barium is opaque to x-rays and blocks their passage. A "barium enema" can be used in a similar way to image the shape of the colon (Ibe *et al.,* 2016). The oil and gas industry is the primary user of barite worldwide. There it is used as a weighting agent in drilling mud. This is a growth industry, as global demand for oil and natural gas has been on a long-term increase. In addition, the long-term drilling trend is more feet of drilling per barrel of oil produced. This has caused the price of barite to increase. Price levels during 2012 were between 10.0% and 20.0% higher than 2011 in many important markets. The typical price of drilling mud barite is about $150 per metric ton at the mine (Cheraghian *et al.,* 2018).

Substitutes for barite in drilling mud include Celestite, Ilmenite, iron ore, and synthetic hematite. None of these substitutes have been effective at displacing barite in any major market area. They are too expensive or do not perform competitively (Tanko *et al.*, 2015). China and India are the leading producers of barite, and they also have the largest reserves. The United States does not produce enough barite to supply its domestic needs. In 2011 the United States produced about 700,000 metric tons of barite and imported about 2,300,000 metric tons (Cheraghian *et al.,* 2018).

Other Uses: Barite is also used in a wide variety of other applications including plastics, clutch pads, rubber mud flaps, mould release compounds, radiation shielding, television and computer monitors, sound-deadening material in automobiles, traffic cones, brake linings, paint and golf balls (Abdou *et al.*, 2018).

2.2 **Techniques for Barite Mining**

2.2.1 **Open Pit Barite Mining**

Open pit mining of barite ore bodies is generally no different than most other open pit mining environments as shown in (Plate I). As in all other sectors of the mining industry, the increasing costs of labour and the decreasing trend in productivities will dictate the use of ever larger and more productive mining equipment (Ezekwesili *et al*., 2012).

Just 10 years ago 4 cu-yd. loaders and 20-25 ton trucks were the largest sizes commonly employed by barite producers. D8's were generally the largest dozers used. Today 35-40 ton trucks with 7-8 cu.yd. Loaders are common (Tanko *et al.,* 2015). The next generation will see the larger surface mines employing 50-60ton haul units coupled with 8-10 cu yd. Loaders (Cheraghian *et al.,* 2018).

Generally speaking, most barite ore bodies amenable to open pit methods are of the size where flexibility of equipment employed is of prime importance. It is common practice to use the same equipment for both stripping and mining, thus permitting much greater flexibility in day-to-day operations, generally better equipment utilization, and commonly lower equipment acquisition and maintenance costs (Mgbemere *et al*., 2018).

Stripping ratios of surface barite mines are increasing and the movement of large volumes of overburden are becoming more and more critical to the overall economics of an operation. One could initially conclude that the higher efficiency of scrappers, draglines, or shovels for overburden removal and truck barite ore bodies are not amenable to using scrappers, draglines or large shovels for the actual mining phase and the ore must be selectively mined at least to the extent that larger stripping equipment would create unacceptable mining dilution. Likewise, many barite ore bodies do not lend themselves to continuous, simultaneous mining and stripping. The flexibility afforded by truck-loader congurations generally outweighs the loss of productivity over scrappers. Most barite ore bodies lend themselves best to cycles of mining and stripping. Together with market, weather, and geological conditions, the flexibility of readily switching from mining to stripping or back to mining generally provides the best possible utilization of manpower and equipment (Abdou *et al.,* 2018)

As the higher grade, larger barite ore bodies become depleted, deeper lower grade ore bodies will naturally be exploited, and the prime consideration in mining will become the removal of larger volumes of material at the least possible cost. Selective mining reduces productivities in any given situation. The greater the degree of this selectivity the lower are resultant productivities and resultant costs can escalate rapidly. The trend now and in the future will be to less selectivity in mining with consequent improvement and enlargement of the beneficiation sector to offset the increased dilution from mining (Cheraghian *et al.,* 2018).

The key to low cost mining and stripping is volume; the greatest amount of material moved in the least amount of time. Increased equipment size with its inherent increased productivities coupled with improved, larger crushing and beneficiation facilities will become the norm in the mining of large barite ore bodies (Giebel *et al.,* 2017).

Plate I: Open Pit Barite Mining Process (Mgbemere *et al*., 2018)

2.2.2 Underground barite mining

Economic exploitation of barite ore bodies by underground methods in the United States and Canada at today's economics would be most difficult if not impossible (Tanko *et al.*, 2015). As alluded to earlier, the large underground barite mines at Malvern, Arkansas and Walton, Nova Scotia were most unique. Most barite ore bodies do not occur in sufficient size or grade to permit underground mining with methods that lend themselves to high productivity mining techniques. Both the Malvern and Walton ore bodies were exceptions. Both were multimillion ton ore bodies of sufficient tonnage and dimension to permit exploitation by highly productive mining methods (Abdou *et al.,* 2018).

Unfortunately, the vast majority of barite occurs in narrow veins of varying degrees of strike and dip and lend themselves only to mining by lower-productivity, narrow-vein-type mining systems. Fortunately, most barite ore-bodies are competent and occur in relatively competent geologic environments. This is a great familiarity with attempts to undercut and block-cave barite, but the extreme competency of the barite prevented natural caving even after massive undercutting of the ore zone (Singh *et al*., 2018).

Open storing and shrink-stopping methods are commonly employed, and technical problems are generally no more complicated than encountered in most other narrow vein mines. Competency of the ore-body, hanging and footwall, together with mine water will be the most important considerations. Extensive support systems and the handling of appreciable water volumes will obviously seriously impact mining costs. Narrow vein barite mines are not large producers. One of the most common problems in narrow vein systems is under-development (Mgbemere *et al*., 2018).

Mining volumes are in direct proportion to the number of people that can be efficiently employed within a mine. Consequently, the number of working faces available within a mine system relates directly to the capacity of that system. Generally speaking, it can and normally does take up to or over a year from primary development of a stopped to final ore extraction in a shrink-stopping operation (Gill *et al.,* 2016).

Annual production is dependent on the number of stopes that can be developed, mined and pulled in a year. Generally narrow vein barite mines are not or cannot be developed to the level required for large volumes. Unless multiple working faces are created by multiple level developments within the same or closely associated vein systems, sufficient stopes cannot be developed to allow continuous, high volume production (Chen *et al.,* 2017).

Under-development creates periods of low production during development cycles, followed by spurts of production when stopes are mined and pulled, again to be followed by low production periods when the mine again has to “catch-up” with development. This can create havoc with costs not only in mining but in all phases of the operation through marketing. Being mined are of sufficient quality to require little or no beneficiation and resultant costs are competitive (Abdou *et al.,* 2018).

Many of these mines are being forced to improve productivities and have remained competitive only by virtue of conversion to the more productive trackless systems employing large, fast, rubber-tired underground equipment. Narrow-vein underground mining of barite requiring extensive beneficiation in order to produce marketable quality material would in most cases be prohibitive at today’s economics (Labe *et al*., 2018).

2.2.3 General Considerations

The single most important factor associated with the development and mining of a barite ore body is people. Generally speaking, approximately 50Å of the cost of barite mining is labour cost. Naturally, this will vary but is generally a workable “rule of thumb.” Not only is the direct cost of labour important but, in certain situations, the indirect costs of labour become virtually prohibitive. A certain percentage of the labour force in all mining situations must be skilled and in the more remote locations of the world the costs of labour can become one of the most important factors in the economics of a barite property. Unlike the ferrous and non-ferrous metals industry, barite mines are extremely small in comparison (the largest in the world are commonly less than 500,000 tons per year capacity) and infrastructure costs of housing and facilities can become prohibitive (Mgbemere *et al.*, 2018). The recent proliferations of governmental regulatory interference in all phases of industry are impacting costs in all areas. Safety, environmental, and permitting regulations on both the federal and state levels are significantly lowering productivities of barite mining. As barite mines are small in comparison to most mines, the impact of recent training regulations and punitive fines on the part of MSHA will have a greater effect on unit costs of production. The days of "throwing together" a small producing unit at nominal cost have just about had it. With stringent noise, dust, safety, training and permitting regulations, the costs of "getting in" to production are much greater, the reserves must be sufficient to justify the initial capital and preproduction development costs and production volumes must be large enough to offset, on a unit cost basis, the impact of the recent proliferation of "zero-productivity" cost impacts (Abdou *et al.*, 2018).

Plate II: Surface Barite Ore Mining (Mgbemere *et al.*, 2018)

2.2.4 Research Gap

Table 2.2: Showing Research Gap in Azara Barite Beneficiation

Thesis Title	Author’s	Findings/Remarks
1. Beneficiation of Azara Barite Ore using combination of Jigging, Froth Flotation and Leaching Method.	1. H. E. Mgbemere, E. O. Obidiegwu and E. Obareki 2018.	1). The work concentrate only in getting Nigeria barite without comparing it with imported barite. 2). It does not explain percentage purity of the barite ore.
2. Characterization and Suitability of Nigerian Barites for Different Industrial Applications.	**2. I**tohan Otoijamun, Moses Kigozi, Adelana Rasak Adetunji and Peter Azikiwe Onwualu 2020.	1). The authors based their findings on characterizing the barite in different locations in Nigeria but couldn’t compare the ones been imported. 2). No work reveal drilling fluid
3. Characterization of barite reserves in Nigeria for use as weighting agent in drilling fluid.	3. David Oluwasegun Afolayan, Adelana Rasak Adetunji, Azikiwe Peter Onwualu, Oghenerume Ogolo and Richard Kwasi Amankwah 2021.	1). No basis on comparison of the barite. 2). No formulation of fluid discussed

2.3.1 **Barite as Drilling Mud**

2.3.2 **Principle Concerning Barite as Drilling Mud**

Drilling-grade barite is produced from commercial barium sulphate-containing ores. The manufacturer retained certificates of analysis or similar documentation on these commercial barium sulphate ores. It may be produced from a single ore or a blend of ores and may be a straight-mined product or processed by beneficiation methods, that is, washing, tabling, jigging or flotation. It may contain accessory minerals in addition to the barium sulphate ($BaSO_4$) mineral. Because of mineral impurities, commercial barite can vary in colour from off-white to grey to red or brown. Common accessory minerals are silicates, such as quartz and chert, carbonate compounds such as siderite and dolomite, and metallic oxide and sulphide compounds. Although these minerals are normally insoluble, they can, under certain conditions, react with other components in some types of drilling fluids and cause adverse changes in the drilling fluid properties (ISO 13500:2008E).

2.3.3 **Mineral Impurities in Barite**

The presence of certain accessory materials in a barite can produce undesirable performance in some drilling fluids. These accessory materials include naturally occurring minerals, such as gypsum, siderite, dolomite and pyrrhotite. gypsum is somewhat soluble in water and releases ions of calcium, one of the alkaline earth metals that are covered in this International Standard (Johnson *et al.*, 2017). Other minerals such as siderite, dolomite and pyrrhotite are not covered in this International Standard, but can cause undesirable performance in some drilling fluids (Cheng *et al.*, 2017). These minerals, though not soluble in water to a significant degree, can release their anions in the presence of hydroxyl ions. Carbonate ions are released from siderite and dolomite in the presence of hydroxyl ions, and sulfide ions are released from pyrrhotite at high temperature in combination with high pH. Because of the conditions under which these minerals are solubilized, not all drilling fluids are detrimentally affected by their presence (Abdou *et al.,* 2018).

Consequently, International Standards limiting their concentrations in barite have not been developed. When it is suspected that one or more is/are affecting mud performance, procedures for determining their concentration in the barite can be found in API RP 13K (ISO 13500:2008E).

Drilling-grade barite be deemed to meet the requirements of the International Standard if a composite sample representing no more than one day's production conforms to the chemical and physical specifications of Table 2.2, represents the product produced and is controlled by the manufacturer (ISO 13500:2008E).

Table 2.3: Barite physical and chemical requirement (ISO 13500:2008E)**.**

Requirement	Standard
Density	4.20 g/ml, minimum
Water-soluble alkaline earth metals, as Calcium	250 mg/kg, maximum
Residue greater than 75 µm	Maximum mass fraction 3.0 %
Particles less than 6 µm in equivalent spherical diameter	Maximum mass fraction 30 %

2.4 **Methods of Beneficiating Barite**

2.4.1 **Gravity Separation**

For the gravity separation of barite, the process involved crushing, screening and jigging. Then the high grade (over 80.0%) concentrate will be produced. Jig is the main equipment for the separation and purification of barite ore, which is energy saving, high efficiency, and environment protection. In the process of crushing, jaw crusher was used and applies two-stage crushing process. In the process of screening, simple and useful circular vibrating screen, which also have the features of large capacity, high efficiency, and convenient operation. It is very suitable for screening of barite ore. In the process of jigging, two kinds of jigs were applied to respectively separate the coarse and fine granularity of barite material (Cheraghian *et al.,* 2018).

2.4.2 **Magnetic Separation**

Wet magnetic separation is usually applied to beneficiate some iron-bearing mineral, like siderite, which applies to barite ore that is used in barium-based medicine requiring low iron barite (Grigorova *et al.,* 2015).

2.4.3 **Froth Flotation**

Is a process for selectively separating hydrophobic materials from hydrophilic. This is used in mineral processing, paper recycling and waste-water treatment industries. Historically this was first used in the mining industry, where it was one of the great enabling technologies of the 20th century. It has been described as "the single most important operation used for the recovery and upgrading of sulphide ores" (Muhammad *et al.,* 2017).

The development of froth flotation has improved the recovery of valuable minerals, such as copper- and lead-bearing minerals. Along with mechanized mining, it has allowed the economic recovery of valuable metals from much lower grade ore than previously (Muhammad *et al.*, 2017).

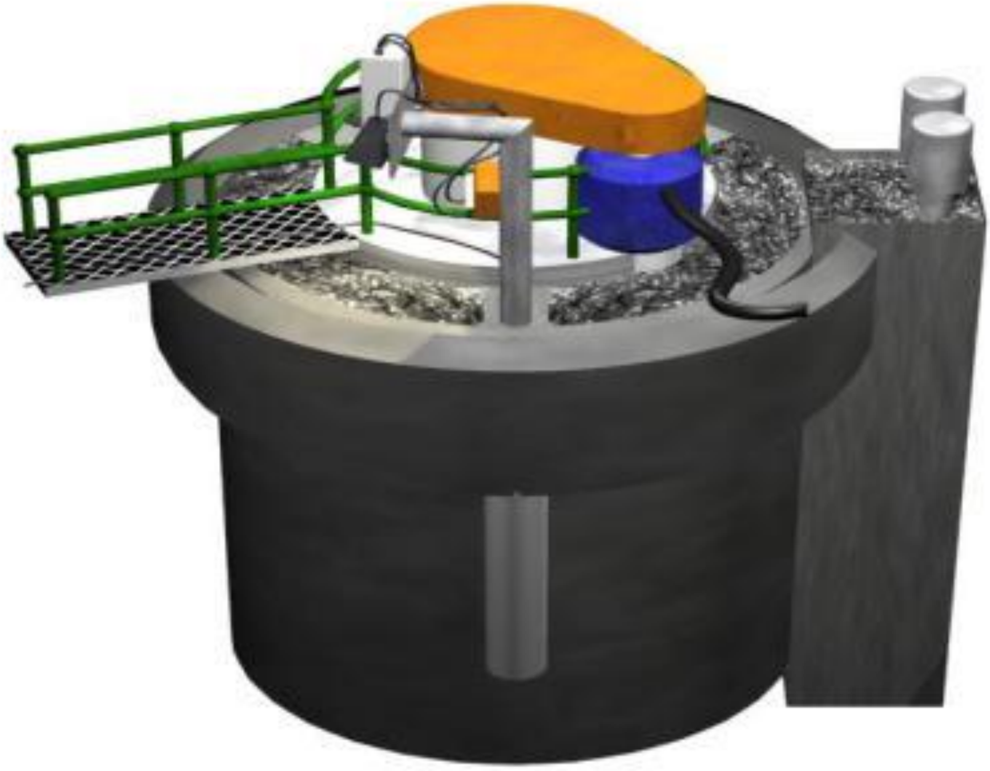

Figure 2.1: Illustrates cylindrical froth flotation cell (Cheraghian *et al.*, 2018)

As for the barite with fine particle size and gravity tailings, we applies process of floatation. According to the different adsorption manner, we use some anionic collector, like fatty acid alkyl sulphate, alkyl sulphonate, or cationic collector, like amide collectors to do the floatation for barite ore (Cheraghian *et al.*, 2018).

2.4.4 **Principle of Operation**

Froth flotation can work, the ore to be treated is reduced to fine particles by crushing and grinding (a process known as comminution) so that the various minerals exist as physically separate grains. This process is known as liberation. The particle sizes are typically less than 0.1 mm (100 µm), but sometimes sizes smaller than 7–10 µm are required (Johson *et al*., 2017). There is a tendency for the liberation size of the minerals to decrease over time as the ore bodies with coarse mineral grains that can be separated at larger sizes are depleted and replaced by ore bodies that were formerly considered too difficult. In the mining industry, the plants where flotation is undertaken to concentrate ore are generally known as concentrators or mills (Labe *et al*., 2018). For froth flotation, the ground ore is mixed with water to form a slurry and the desired mineral is rendered hydrophobic by the addition of a surfactant or collector chemical (although some mineral surfaces are naturally hydrophobic requiring little or no addition of collector) (Jehlička *et al*., 2009). The particular chemical depends on the nature of the mineral to be recovered and, perhaps, the natures of those that are not wanted. As an example, sodium ethyl xanthate may be added as a collector in the selective flotation of galena (lead sulphide) to separate it from sphalerite (zinc sulphide). This slurry (more properly called the pulp) of hydrophobic particles and hydrophilic particles is then introduced to tanks known as flotation cells that are aerated to produce bubbles. The hydrophobic particles attach to the air bubbles, which rise to the surface, forming froth the froth is removed from the cell, producing a concentrate ("con") of the target mineral. Frothing agents, known as frothers, may be introduced to the pulp to promote the formation of a stable froth on top of the flotation cell (Abdou *et al.,* 2018). The minerals that do not float into the froth are referred to as the flotation tailings or flotation tails. These tailings may also be subjected to further stages of flotation to recover the valuable particles that did not float the first time. This is known as scavenging. The final tailings after scavenging are normally pumped for disposal as mine fill or to tailings disposal facilities for long-term storage (Ibe *et al*., 2016).

Froth flotation efficiency is determined by a series of probabilities: those of particle–bubble contact, particle–bubble attachment, transport between the pulp and the froth, and froth collection into the product launder (Antao, 2012).

In a conventional mechanically-agitated cell, the void fraction (that is, volume occupied by air bubbles) is low (5 to 10 per cent) and the bubble size is usually greater than 1 mm. This results in a relatively low interfacial area and a low probability of particle–bubble contact. Consequently, several cells in series are required to increase the particle residence time, thus increasing the probability of particle–bubble contact (labe *et al*., 2018).

Flotation is normally undertaken in several stages to maximize the recovery of the target mineral or minerals and the concentration of those minerals in the concentrate, while minimizing the energy input (Duru *et al.,* 2019).

2.4.5 Flotation Stages

2.4.5.1 Roughing

The first stage is called roughing, which produces a rougher concentrate. The objective is to remove the maximum amount of the valuable mineral at as coarse a particle size as practical. The finer an ore is ground, the greater the energy that is required, so it makes sense to fine grind only those particles that need fine grinding. Complete liberation is not required for rougher flotation, only sufficient liberation to release enough gangue from the valuable mineral to get a high recovery (Wang *et al.,* 2014).

The primary objective of roughing is to recover as much of the valuable minerals as possible, with less emphasis on the quality of the concentrate produced (Markl *et al*., 2018). In some concentrators, there may be a pre-flotation step that precedes roughing. This is done when there are some undesirable materials, such as organic carbon, that readily float. They are removed first to avoid them floating during roughing (and thus contaminating the rougher concentrate (Abdou *et al.,* 2018).

2.4.5.2 Cleaning

The rougher concentrate is normally subjected to further stages of flotation to reject more of the undesirable minerals that also reported to the froth, in a process known as cleaning. The product of cleaning is known as the cleaner concentrate or the final concentrate. The objective of cleaning is to produce as high a concentrate grade as possible (Labe *et al*., 2018).

The rougher concentrate is often subject to further grinding (usually called regrinding) to get more complete liberation of the valuable minerals. Because it is a smaller mass than that of the original ore, less energy is needed than would be necessary if the whole ore were reground. Regrinding is often undertaken in specialized regrind mills, such as the Isa-Mill, designed to further reduce the energy consumed during regrinding to finer sizes (Wang *et al.,* 2014).

2.4.5.3 Scavenging

The rougher flotation step is often followed by a scavenger flotation step that is applied to the rougher tailings. The objective is to recover any of the target minerals that were not recovered during the initial roughing stage. This might be achieved by changing the flotation conditions to make them more rigorous than the initial roughing, or there might be some secondary grinding to provide further liberation (Labe *et al*., 2018).

The concentrate from the rougher scavengers could be returned to the rougher feed for re-floating or sent to special cleaner cells. Similarly, the cleaning step may also be followed by a scavenging step performed on the cleaner tailings (Mgbemere *et al*., 2018).

2.4.6 Science of Flotation

To be effective on a given ore slurry, the collectors are chosen based upon their selective wetting of the types of particles to be separated. A good collector will adsorb, physically or chemically, with one of the types of particles. This provides the thermodynamic requirement for the particles to bind to the surface of a bubble. The wetting activity of a surfactant on a particle can be quantified by measuring the contact angles that the liquid/bubble interface makes with it. Another important measure for attachment of bubbles to particles is induction time. The induction time is the time required for the particle and bubble to rupture the thin film separating the particle and bubble. This rupturing is achieved by the surface forces between the particle and bubble (Markl *et al*., 2018).

The mechanism for the bubble-particle attachment is very complex and consists of three steps, collision, attachment and detachment. The collision is achieved by particles being within the collision tube of a bubble and this is affected by the velocity of the bubble and radius of the bubble. The collision tube corresponds to the region in which a particle will collide with the bubble, with the perimeter of the collision tube corresponding to the grazing trajectory (Labe *et al*., 2018).

The attachment of the particle to the bubble is controlled by the induction time of the particle and bubble. The particle and bubble need to bind and this occurs if the time in which the particle and bubble are in contact with each other is larger than the required induction time. This induction time is affected by the fluid viscosity, particle and bubble size and the forces between the particle and bubbles (Winter, 2017). The detachment of a particle and bubble occurs when the force exerted by the surface tension is exceeded by shear forces and gravitational forces. These forces are complex and vary within the cell. High shear will be experienced close to the impeller of a mechanical flotation cell and mostly gravitational force in the collection and cleaning zone of a flotation column. Significant issues of entrainment of fine particles occurs as these particles experience low collision efficiencies as well as sliming and degradation of the particle surfaces. Coarse particles show a low recovery of the valuable mineral due to the low liberation and high detachment efficiencies (Olamilekan *et al.,* 2020).

2.4.7 Flotation Theory

2.4.7.1 Selective Adhesion

Froth flotation depends on the selective adhesion of air bubbles to mineral surfaces in mineral/water slurry. The air bubbles will attach to more hydrophobic particles. The attachment of the bubbles to the surface is determined by the interfacial energies between the solid, liquid, and gas phases. This is determined by the Young-Dupre Equation: (Kawatra *et al.,* 2015).

$$\gamma\text{lv}\,COS\theta = (\gamma\text{sv} - \gamma\text{sl}) \tag{2.1}$$

Where:

γlv is the surface energy of the liquid/vapour interface

γsv is the surface energy of the solid/vapour interface

γsl is the surface energy of the solid/liquid interface,

θ is the contact angle, the angle formed at the junction between vapour, solid, and liquid phases (Singh *et al.*, 2006)

Minerals targeted for separation may be chemically surface-modified with collectors so that they are more hydrophobic see (Figure 2.2). Collectors are a type of surfactant that increases the natural hydrophobicity of the surface, increasing the separatability of the hydrophobic and hydrophilic particles. Collectors either chemically bond via chemisorption to the mineral or adsorb onto the surface via physio-sorption (Markl *et al.*, 2019).

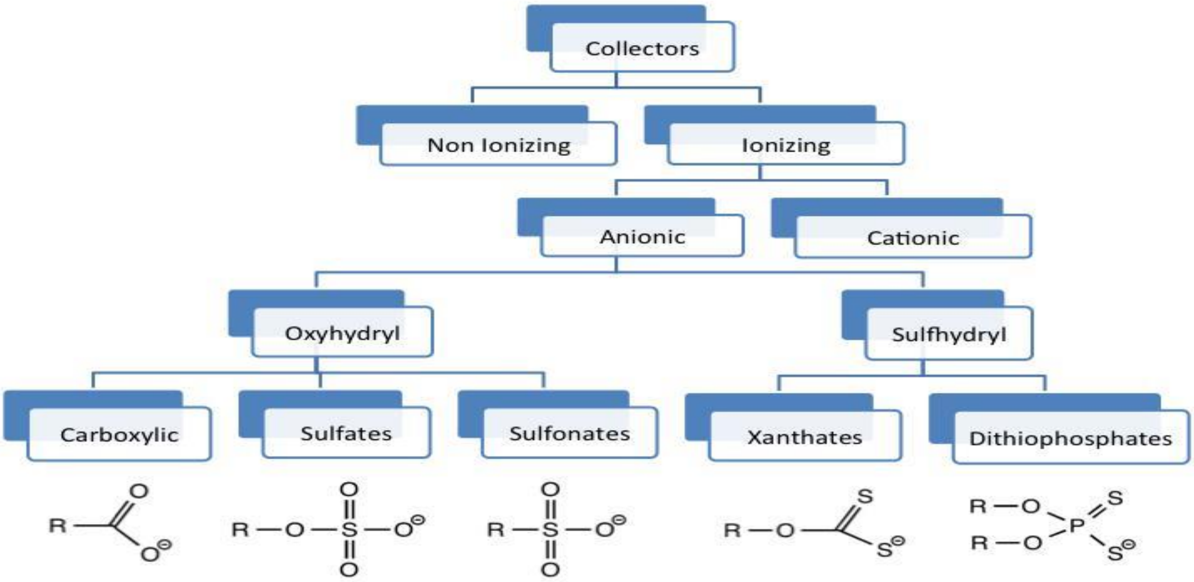

Figure 2.2: Different types of collectors or surfactants used in froth flotation (Cheraghian *et al.*, 2018)

2.4.7.2 Collision

The collision rates for fine particles (50 - 80 µm) can be accurately modelled, but there is no current theory that accurately models bubble-particle collision for particles as large as 300 µm, which are commonly used in flotation processes (Cheraghian *et al.,* 2018).

For fine particles, Stokes law underestimates collision probability while the potential equation based on surface charge overestimates collision probability so an intermediate equation is used (Markl *et al.,* 2019) It is important to know the collision rates in the system since this step precedes the adsorption where a three phase system is formed (Labe *et al*., 2018).

2.4.7.3 Adsorption

The effectiveness of a medium to adsorb a particle is influenced by the relationship between the surfaces of both materials. There are multiple factors that affect the efficiency of adsorption in chemical, thermodynamic, and physical domains. These factors can range from surface energy and polarity to the shape, size, and roughness of the particle. In froth flotation, adsorption is a strong consequence of surface energy, since the small particles have a high surface area to size ratio, resulting in higher energy surfaces to form attractions with adsorbates. The air bubbles must selectively adhere to the desired minerals to elevate them to the surface of the slurry while wetting the other minerals and leaving them in the aqueous slurry medium (Olamilekan *et al.,* 2020).

Particles that can be easily wetted by water are called hydrophilic, while particles that are not easily wetted by water are called hydrophobic. Hydrophobic particles have a tendency to form a separate phase in aqueous media. In froth flotation the effectiveness of an air bubble to adhere to a particle is based on how hydrophobic the particle is. Hydrophobic particles have an affinity to air bubbles, leading to adsorption. The bubble-particle combinations are elevated to the froth zone driven by buoyancy forces (Kawatra *et al.*, 2015).

The attachment of the bubbles to the particles is determined by the interfacial energies of between the solid, liquid, and vapour phases, as modelled by the Young/Dupre Equation. The interfacial energies can be based on the natural structure of the materials, or the addition of chemical treatments can improve energy compatibility (Nzeh *et al.*, 2018).

Collectors are the main additives used to improve particle surfaces. They function as surfactants to selectively isolate and aid adsorption between the particles of interest and bubbles rising through the slurry. Common collectors used in flotation are anionic sulphur ligands, which have a bi-functional structure with an ionic portion which shares attraction with metals, and a hydrophobic portion such as a long hydrocarbon tail. These collectors coat a particle's surface with a monolayer of non-polar substance to aid separation from the aqueous phase by decreasing the adsorbed particle solubility in water. The adsorbed ligands can form micelles around the particles and form small-particle colloids improving stability and phase separation further (Olamilekan *et al.,* 2020).

The adsorption of particles to bubbles is essential to separating the minerals from the slurry, but the minerals must be purified from the additives used in separation, such as the collectors, frothers, and modifiers. The product of the cleaning, or desorption process, is known as the cleaner concentrate. The detachment of a particle and bubble requires adsorption bond cleavage driven by shear forces. Depending on the flotation cell type, shear forces are applied by a variety of mechanical systems. Among the most common are impellers and mixers. Some systems combine the functionalities of these components by placing them at key locations where they can take part in multiple froth flotation mechanisms. Cleaning cells also take advantage of gravitational forces to improve separation efficiency (Winter, 2017).

2.4.7.4 Desorption (Detachment)

The adsorption of particles to bubbles is essential to separating the minerals from the slurry, but the minerals must be purified from the additives used in separation, such as the collectors, frothers, and modifiers. The product of the cleaning, or desorption process, is known as the cleaner concentrate (Olamilekan *et al.,* 2020).

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2.4.8 **Performance Calculation**

2.4.8.1 ***Relevant Equations***

A common quantity used to describe the collection efficiency of a froth flotation process is flotation recovery (R). This quantity incorporates the probabilities of collision and attachment of particles to gas flotation bubbles (Winter, 2017).

$$R = \frac{Nc}{(\frac{\pi}{4})(\mathrm{dp} + \mathrm{db})2\mathrm{Hc}} \qquad (2.2)$$

Where:

$N_c = PN_c^i$, Which is the product of the probability of the particle being collected (P) and the number of possible particle collisions ($N^i c$) (Achusim-Udenko *et al*., 2019).

dp is particle diameter

db is bubble diameter

H is a specified height within the flotation which the recovery was calculated

C is the particle concentration

The following, are several additional mathematical methods often used to evaluate the effectiveness of froth flotation processes. These equations are simpler than the calculation for flotation recovery, as they are based solely on the amounts of inputs and outputs of the processes (Gill *et al.*, 2016).

For equations (2.3, 2.6):

F is the weight per cent of feed

C is the weight per cent concentrate

T is the weight per cent of tailings

c, *t*, and *f* are the metallurgical assays of the concentrate, tailings, and feed, respectively

Ratio of feed weight to concentrate weight F/C (unit less)

$$\frac{F}{C} = \frac{c-t}{f-t} \tag{2.3}$$

2.4.8.2 Per cent of metal recovered (X_R) in wt%

$$XR = 100\left(\frac{c}{f}\right)\left(\frac{f-t}{c-t}\right) \tag{2.4}$$

Percent of metal lost (XL) in wt%

$$XL = 100 - XR$$

Percent of weight recovered (X_W) in wt%

$$XW = 100 \left(\frac{C}{F}\right) = 100\ \frac{f-t}{c-t} \qquad (2.5)$$

2.4.8.3 Grade-Recovery

Grade-recovery curves in figure 2.3 are useful tools in weighing the trade-off of producing a high grade of concentrate while maintaining as low of a recovery rate as possible, two important aspects of froth flotation. These curves are developed empirically based on the individual froth flotation process of a particular plant. As the curves are shifted in the positive x-direction (to the right) and the positive y-direction (upward) the performance of the froth flotation process is regarded as improving. A disadvantage to these curves is that they can only compare the grade-recovery relations of a specific feed grade and feed rate. If a company has a variance of feed grades and rates used (an extremely common occurrence) in their froth flotation process, grade-recovery curves for every pairing of feed grade and recovery rate would have to be constructed in order to provide meaningful information to the plant (Giebel *et al*., 2017).

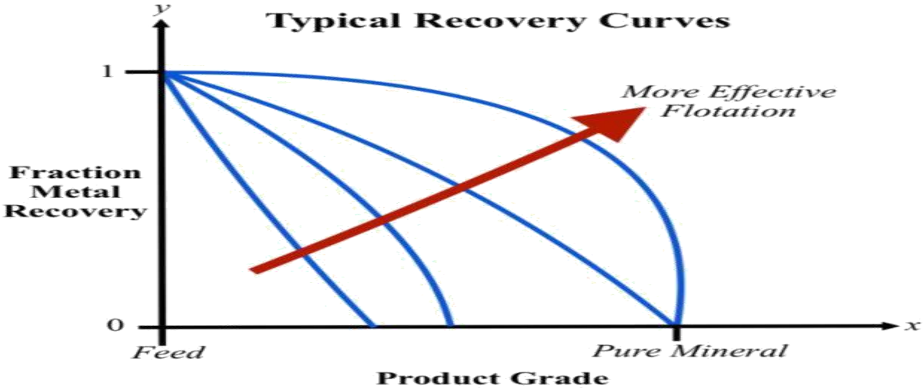


Figure 2.3: Grade-recovery relationships seen in froth flotation (Giebel *et al*., 2017)

2.5 **Flotation Equipment**

Flotation can be performed in rectangular or cylindrical mechanically agitated cells or tanks, flotation columns, Jameson Cells or deinking flotation machines shown in figure 2.4. Classified by the method of air absorption manner, it is fair to state that two distinct groups of flotation equipment have arisen: pneumatic and mechanical machines. Generally pneumatic machines give a low-grade concentrate and little operating troubles comparison of the sizes of flotation columns and Jameson Cells with similar capacities (Olamilekan *et al.,* 2020).

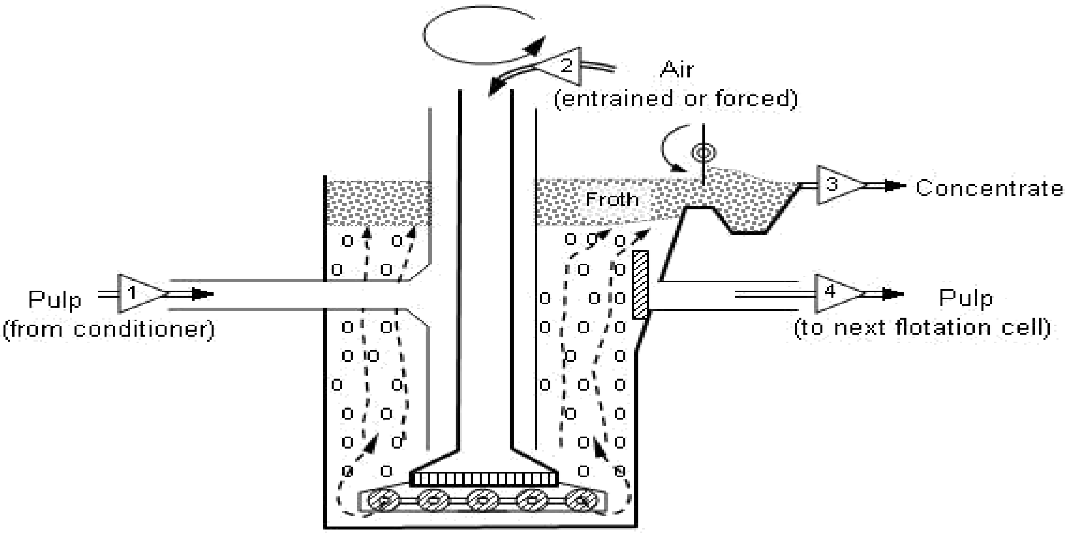


Figure 2.4: Barite Ore Flotation cell (Grigorova *et al.*, 2015)

Mechanical cells use a large mixer and diffuser mechanism at the bottom of the mixing tank to introduce air and provide mixing action. Flotation columns use air spargers to introduce air at the bottom of a tall column while introducing slurry above. The counter-current motion of the slurry flowing down and the air flowing up provides mixing action. Mechanical cells generally have a higher throughput rate, but produce material that is of lower quality, while flotation columns generally have a low throughput rate but produce higher quality material the Jameson cell uses neither impellers nor spargers, instead combining the slurry with air in a downcomer where high shear creates the turbulent conditions required for bubble particle contacting (Grigorova *et al.*, 2015).

2.5.1 **Mechanics of Flotation**

The following steps are followed, following grinding to liberate the mineral particles:

1. Reagent conditioning to achieve hydrophobic surface charges on the desired particles
2. Collection and upward transport by bubbles in an intimate contact with air or nitrogen
3. Formation of a stable froth on the surface of the flotation cell
4. Separation of the mineral laden froth from the bath (flotation cell) (Winter, 2017).

Numbered triangles show direction of stream flow. Various flotation reagents are added to a mixture of ore and water (called pulp) in a conditioning tank. The flow rate and tank size are designed to give the minerals enough time to be activated. The conditioner pulp (Jameson, 1992), is fed to a bank of rougher cells which remove most of the desired minerals as a concentrate. The rougher pulp (Grigorova et *al.*, 2015) passes to a bank of scavenger cells where additional reagents may be added. The scavenger cell froth is usually returned to the rougher cells for additional treatment, but in some cases may be sent to special cleaner cells. The scavenger pulp is usually barren enough to be discarded as tails. More complex flotation circuits have several sets of cleaner and re-cleaner cells, and intermediate re-grinding of pulp or concentrate as shown in figure 2.5 (Grigorova *et al.*, 2015).

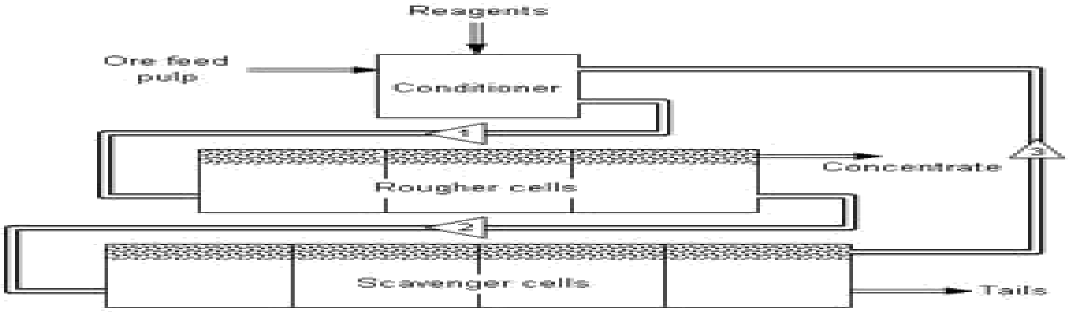


Figure: 2.5: Simple flotation circuit for mineral concentration (Grigorova et *al.*, 2015)

2.5.2 **Chemical of Flotation**

2.5.2.1 Collectors

For many ores (for instance, those of Cu, Mo, W, Ni, Ba), the collectors are anionic sulphur ligands. Particularly popular are xanthate salts, including potassium amyl xanthate (PAX), potassium isobutyl xanthate (PIBX), potassium ethyl xanthate (KEX), sodium isobutyl xanthate(SIBX), sodium isopropyl xanthate (SIPX), sodium ethyl xanthate (SEX). Other collectors include related sulphur-based ligands: dithiophosphates, dithiocarbamates. Still other classes of collectors include the thiourea thiocarbanilide. Fatty acids (oleic acid) have also been used. For some minerals (for example, sylvanite for KCl), fatty amines are used as collectors (Grigorova et *al.*, 2015).

2.5.2.2 Frothers

A variety of compounds are added to stabilize the foams. These additives include pine oil, various alcohols (methyl isobutyl carbinol (MIBC)), polyglycols, xylenol (cresylic acid).

2.5.2.3 Modifier

A variety of other compounds are added to optimize the separation process these additives are called modifiers. Such species do not interact directly with the mineral, but modify the physical properties of the solution.

pH modifiers include lime (CaO), Soda ash (Na_2CO_3), Caustic soda (NaOH), sulphuric and hydrochloric acid (H_2SO_4, HCl).

Anionic modifiers include phosphates, silicates, and carbonates.

Organic modifiers include the thickeners dextrin, starch, glue, and CMC (Winter, 2017).

2.6 Drilling Mud

In geotechnical engineering, drilling fluid, also called drilling mud, is used to aid the drilling of boreholes into the earth. Often used while drilling oil and natural gas wells and on exploration drilling rigs, drilling fluids are also used for much simpler boreholes, such as water wells. One of the functions of drilling mud is to carry cuttings out of the hole (Chen *et al.,* 2017).

The three main categories of drilling fluids are: water-based muds (WBs), which can be dispersed and non-dispersed; non-aqueous muds, usually called oil-based muds (OBs); and gaseous drilling fluid, in which a wide range of gases can be used. Along with their formatives, these are used along with appropriate polymer and clay additives in (plate iii), for drilling various oil and gas formations (Cheraghain *et al*., 2018).

The main functions of drilling fluids include providing hydrostatic pressure to prevent formation fluids from entering into the well bore, keeping the drill bit cool and clean during drilling, carrying out drill cuttings, and suspending the drill cuttings while drilling is paused and when the drilling assembly is brought in and out of the hole. The drilling fluid used for a particular job is selected to avoid formation damage and to limit corrosion (Winter, 2017).

Plate III: Barite powder used for preparation of water-based mud (Cheraghain *et al*., 2018)

2.6.1 Types of Drilling Mud

Many types of drilling fluids are used on a day-to-day basis. Some wells require that different types be used at different parts in the hole, or that some types be used in combination with others. The various types of fluid generally fall into a few broad categories (Langewiesche, 2017).

Air: Compressed air is pumped either down the bore hole's annular space or down the drill string itself.

Air/water: The same as above, with water added to increase viscosity, flush the hole, provide more cooling, and/or to control dust.

Air/polymer: A specially formulated chemical, most often referred to as a type of polymer, is added to the water and air mixture to create specific conditions. A foaming agent is a good example of a polymer.

Water: Water by itself is sometimes used. In offshore drilling sea water is typically used while drilling the top section of the hole (Strbac *et al*., 2018).

Water-based mud (WBM): Most basic water-based mud systems begin with water, then clays and other chemicals are incorporated into the water to create a homogeneous blend resembling something between chocolate milk and a malt (depending on viscosity). The clay is usually a combination of native clays that are suspended in the fluid while drilling, or specific types of clay that are processed and sold as additives for the WBM system. The most common of these is bentonite, frequently referred to in the oilfield as "gel". Gel likely makes reference to the fact that while the fluid is being pumped, it can be very thin and free-flowing (like chocolate milk), though when pumping is stopped, the static fluid builds a "gel" structure that resists flow. When an adequate pumping force is applied to "break the gel", flow resumes and the fluid returns to its previously free-flowing state. Many other chemicals (for example, potassium formate) are added to a WBM system to achieve various effects, including: viscosity control, shale stability, enhance drilling rate of penetration, cooling and lubricating of equipment (Winter, 2017).

Oil-based mud (OBM): Oil-based mud is a mud where the base fluid is a petroleum product such as diesel fuel. Oil-based muds are used for many reasons, including increased lubricity, enhanced shale inhibition, and greater cleaning abilities with less viscosity. Oil-based muds also withstand greater heat without breaking down. The use of oil-based muds has special considerations, including cost, environmental considerations such as disposal of cuttings in an appropriate place, and the exploratory disadvantages of using oil-based mud, especially in wildcat wells. Using an oil-based mud interferes with the geochemical analysis of cuttings and cores and with the determination of API gravity because the base fluid cannot be distinguished from oil returned from the formation (Olamilekan *et al.,* 2020).

Synthetic-based fluid (SBM) (Otherwise known as Low Toxicity Oil Based Mud or LTOBM): Synthetic-based fluid is a mud where the base fluid is a synthetic oil. This is most often used on offshore rigs because it has the properties of an oil-based mud, but the toxicity of the fluid fumes is much less than an oil-based fluid. This is important when men work with the fluid in an enclosed space such as an offshore drilling rig. Synthetic-based fluid poses the same environmental and analysis problems as oil-based fluid (Winter, 2017).

On a drilling rig, mud is pumped from the mud pits through the drill string where it sprays out of nozzles on the drill bit, cleaning and cooling the drill bit in the process. The mud then carries the crushed or cut rock ("cuttings") up the annular space ("annulus") between the drill string and the sides of the hole being drilled, up through the surface casing, where it emerges back at the surface (PEH, 2007). Cuttings are then filtered out with either a shale shaker, or the newer shale conveyor technology, and the mud returns to the mud pits. The mud pits let the drilled "fines" settle; the pits are also where the fluid is treated by adding chemicals and other substances shown in plate iv below (Ezekwesili *et al*., 2012).

The returning mud can contain natural gases or other flammable materials which will collect in and around the shale shaker / conveyor area or in other work areas. Because of the risk of a (Fernández-Remolar, *et al.,* 2018).

Plate IV: Drilling Fluid Pit (Langewiesche, 2017)

Fire or an explosion if they ignite, special monitoring sensors and explosion-proof certified equipment is commonly installed, and workers are advised to take safety precautions. The mud is then pumped back down the hole and further re-circulated. After testing, the mud is treated periodically in the mud pits to ensure properties which optimize and improve drilling efficiency, borehole stability, and other requirements (Langewiesche, 2017).

2.6.2 **Function of Drilling Mud**

The main functions of a drilling mud can be summarized as follows:

2.6.2.1 Remove cuttings from the well

Drilling fluid carries the rock excavated by the drill bit up to the surface. Its ability to do so depends on cutting size, shape, and density, and speed of fluid traveling up the well (annular velocity). These considerations are analogous to the ability of a stream to carry sediment; large sand grains in a slow-moving stream settle to the stream bed, while small sand grains in a fast-moving stream are carried along with the water. The mud viscosity is another important property, as cuttings will settle to the bottom of the well if the viscosity is too low (Winter, 2017).

Plate V: Barite Drilling Mud Pit (Cheraghain *et al*., 2018)

Other properties include:

Most drilling muds are thixotropic (viscosity increase during static conditions). This characteristic keeps the cuttings suspended when the mud is not flowing during, for example, maintenance.

Fluids that have shear thinning and elevated viscosities are efficient for hole cleaning.

Higher annular velocity improves cutting transport.

Transport ratio (transport velocity / lowest annular velocity) should be at least 50%. High density fluids may clean hole adequately even with lower annular velocities (by increasing the buoyancy force acting on cuttings).

But may have a negative impact if mud weight is in excess of that needed to balance the pressure of surrounding rock (formation pressure), so mud weight is not usually increased for hole cleaning purposes. Higher rotary drill-string speeds introduce a circular component to annular flow path. This helical flow around the drill-string causes drill cuttings near the wall, where poor hole cleaning conditions occur, to move into higher transport regions of the annulus (Olamilekan *et al.,* 2020).

Increased rotation is the one of the best methods for increasing hole cleaning in high angle and horizontal wells (Winter, 2017).

2.6.2.2 Suspend and Release Cuttings

Must suspend drill cuttings, weight materials and additives under a wide range of conditions. Drill cuttings that settle can causes bridges and fill, which can cause stuck-pipe and lost circulation. Weight material that settles is referred to as sag, this causes a wide variation in the density of well fluid, this more frequently occurs in high angle and hot wells (Olamilekan *et al.,* 2020). High concentrations of drill solids are detrimental to:

i. Drilling efficiency (it causes increased mud weight and viscosity, which in turn increases maintenance costs and increased dilution)
ii. Rate of Penetration (ROP) (increases horsepower required to circulate)
iii. Mud properties that are suspended must be balanced with properties in cutting removal by solids control equipment (Winter, 2017).For effective solids controls, drill solids must be removed from mud on the 1st circulation from the well. If re-circulated, cuttings break into smaller pieces and are more difficult to remove.

Conduct a test to compare the sand content of mud at flow line and suction pit (to determine whether cuttings are being removed) (Winter, 2017).

2.6.2.3 Control Formation Pressure

If formation pressure increases, mud density should also be increased to balance pressure and keep the wellbore stable. The most common weighting material is barite. Unbalanced formation pressures will cause an unexpected influx (also known as a kick) of formation fluids in the wellbore possibly leading to a blowout from pressured formation fluids (Winter, 2017).

Hydrostatic pressure = density of drilling fluid * true vertical depth * acceleration of gravity. If hydrostatic pressure is greater than or equal to formation pressure, formation fluid will not flow into the wellbore.

Well control means no uncontrollable flow of formation fluids into the wellbore.

Hydrostatic pressure also controls the stresses caused by tectonic forces, these may make wellbores unstable even when formation fluid pressure is balanced.

If formation pressure is subnormal, air, gas, mist, stiff foam, or low density mud (oil base) can be used.

In practice, mud density should be limited to the minimum necessary for well control and wellbore stability. If too great it may fracture the formation (Singh *et al*., 2018).

2.6.2.4 Seal Permeable Formations

Mud column pressure must exceed formation pressure, in this condition mud filtrate invades the formation, and a filter cake of mud is deposited on the wellbore wall.

Mud is designed to deposit thin, low permeability filter cake to limit the invasion.

Problems occur if a thick filter cake is formed; tight hole conditions, poor log quality, stuck pipe, lost circulation and formation damage (RMRDC, 2016).

In highly permeable formations with large bore throats, whole mud may invade the formation, depending on mud solids size:

i. Use bridging agents to block large opening, then mud solids can form seal.
ii. For effectiveness, bridging agents must be over the half size of pore spaces/ fractures.
iii. Bridging agents (for example, calcium carbonate and ground cellulose).

Depending on the mud system in use, a number of additives can improve the filter cake (for instance, bentonite, natural and synthetic polymer, asphalt and gilsonite) (Winter, 2017).

2.6.2.5 Maintain Wellbore Stability

Chemical composition and mud properties must combine to provide a stable wellbore. Weight of the mud must be within the necessary range to balance the mechanical forces. Wellbore instability = sloughing formations, which can cause tight hole conditions, bridges and fill on trips (same symptoms indicate hole cleaning problems). Wellbore stability = hole maintains size and cylindrical shape.

If the hole is enlarged, it becomes weak and difficult to stabilize, resulting in problems such as low annular velocities, poor hole cleaning, solids loading and poor formation evaluation in sand and sandstones formations, hole enlargement can be accomplished by mechanical actions (hydraulic forces & nozzles velocities). Formation damage is reduced by conservative hydraulics system. A good quality filter cake containing bentonite is known to limit bore hole enlargement.

In shales, mud weight is usually sufficient to balance formation stress, as these wells are usually stable. With water base mud, chemical differences can cause interactions between mud and shale that lead to softening of the native rock. Highly fractured, dry, brittle shales can be extremely unstable (leading to mechanical problems) (PEH, 2007).

Various chemical inhibitors can control mud/shale interactions (calcium, potassium, salt, polymers, asphalt, glycols and oil–best for water sensitive formations)

Oil (and synthetic oil) based drilling fluids are used to drill most water sensitive Shales in areas with difficult drilling conditions.

To add inhibition, emulsified brine phase (calcium chloride) drilling fluids are used to reduce water activity and creates osmotic forces to prevent adsorption of water by Shales (Labe *et al*., 2018).

2.6.2.6 Minimizing Formation Damage

Skin damage or any reduction in natural formation porosity and permeability (washout) constitutes formation damage

Skin damage is the accumulation of residuals on the perforations and that causes a pressure drop through them.

Most common damage:

i. Mud or drill solids invade the formation matrix, reducing porosity and causing skin effect
ii. Swelling of formation clays within the reservoir, reduced permeability
iii. precipitation of solids due to mixing of mud filtrate and formations fluids resulting in the precipitation of insoluble salts
iv. Mud filtrate and formation fluids form an emulsion, reducing reservoir porosity specially designed drill-in fluids or work over and completion fluids, minimize formation damage (Markl *et al*., 2018).

Cool, Lubricate and Support the Bit and Drilling Assembly

Heat is generated from mechanical and hydraulic forces at the bit and when the drill string rotates and rubs against casing and wellbore.

Cool and transfer heat away from source and lower to temperature than bottom hole.

If not, the bit, drill string and mud motors would fail more rapidly.

Lubrication based on the coefficient of friction. ("Coefficient of friction" is how much friction on side of wellbore and collar size or drill pipe size to pull stuck pipe) Oil- and synthetic-based mud generally lubricate better than water-based mud (but the latter can be improved by the addition of lubricants) (PEH, 2007).

Amount of lubrication provided by drilling fluid depends on type & quantity of drill solids and weight materials + chemical composition of system.

Poor lubrication causes high torque and drag, heat checking of the drill string, but these problems are also caused by key seating, poor hole cleaning and incorrect bottom hole assemblies design. Drilling fluids also support portion of drill-string or casing through buoyancy. Suspend in drilling fluid, buoyed by force equal to weight (or density) of mud, so reducing hook load at derrick. Weight that derrick can support limited by mechanical capacity, increase depth so weight of drill-string and casing increase. When running long, heavy string or casing, buoyancy possible to run casing strings whose weight exceed a rig's hook load capacity (Langewiesche, 2017).

2.6.2.7 Transmit Hydraulic Energy to Tools and Bit

Hydraulic energy provides power to mud motor for bit rotation and for MWD (measurement while drilling) and LWD (logging while drilling) tools. Hydraulic programs base on bit nozzles sizing for available mud pump horsepower to optimize jet impact at bottom well.

Limited to:

i. Pump horsepower

ii. Pressure loss inside drill string

iii. Maximum allowable surface pressure

iv. Optimum flow rate

v. Drill string pressure loses higher in fluids of higher densities, plastic viscosities and solids.

Low solids, shear thinning drilling fluids such as polymer fluids, more efficient in transmit hydraulic energy.

Depth can be extended by controlling mud properties.

Transfer information from MWD and LWD to surface by pressure pulse (Winter, 2017).

2.6.2.8 Ensure Adequate Formation Evaluation

Chemical and physical mud properties as well as wellbore conditions after drilling affect formation evaluation. Mud loggers examine cuttings for mineral composition, visual sign of hydrocarbons and recorded mud logs of lithology, ROP, gas detection or geological parameters. Wireline logging measure electrical, sonic, nuclear and magnetic resonance.Potential productive zone is isolated and performed formation testing and drill stem testing. Mud helps not to disperse of cuttings and also improve cutting transport for mud loggers determine the depth of the cuttings originated. Oil-based mud, lubricants, asphalts will mask hydrocarbon indications.

So mud for drilling core selected based on type of evaluation to be performed (many coring operations specify a blend mud with minimum of additives) (Labe *et al*., 2018).

2.6.2.9 Corrosion Control

Drill-string and casing in continuous contact with drilling fluid may cause a form of corrosion. Dissolved gases (oxygen, carbon dioxide, hydrogen sulfide) cause serious corrosion problems;

i. Cause rapid, catastrophic failure

ii. May be deadly to humans after a short period of time

Low pH (acidic) aggravates corrosion, so use corrosion coupons to monitor corrosion type, rates and to tell correct chemical inhibitor is used in correct amount.

Mud aeration, foaming and other O_2 trapped conditions cause corrosion damage in short period time.

When drilling in high H_2S, elevated the pH fluids + sulfide scavenging chemical (zinc) (Winter, 2017).

2.6.2.10 Facilitate Cementing and Completion

Cementing is critical to effective zone and well completion.

During casing run, mud must remain fluid and minimize pressure surges so fracture induced lost circulation does not occur.

Temperature of water used for cement must be within tolerance of cementers performing task, usually 70 degrees, most notably in winter conditions.

Mud should have thin, slick filter cake, with minimal solids in filter cake, wellbore with minimal cuttings, caving or bridges will prevent a good casing run to bottom. Circulate well bore until clean.

To cement and completion operation properly, mud displace by flushes and cement. For effectiveness;

i. Hole near gauges, use proper hole cleaning techniques, pumping sweeps at TD, and perform wiper trip to shoe.

Mud low viscosity, mud parameters should be tolerant of formations being drilled, and drilling fluid composition, turbulent flow - low viscosity high pump rate, laminar flow - high viscosity, high pump rate (Olamilekan *et al.,* 2020).

2.6.2.11 Minimize Environmental Impact

Mud is, in varying degrees, toxic. It is also difficult and expensive to dispose of it in an environmentally friendly manner. A Vanity Fair article described the conditions at Lago Agrio, a large oil field in Ecuador where drillers were effectively unregulated (Winter, 2017). Water based drilling fluid has very little toxicity, made from water, bentonite and barite, all clay from mining operations, usually found in Wyoming and in Lunde, Telemark. There are specific chemicals that can be used in water based drilling fluids that alone can be corrosive and toxic, such as hydrochloric acid. However, when mixed into water based drilling fluids, hydrochloric acid only decreases the pH of the water to a more manageable level. Caustic (sodium hydroxide), anhydrous lime, soda ash, bentonite, barite and polymers are the most common chemicals used in water based drilling fluids. Oil Base Mud and synthetic drilling fluids can contain high levels of benzene, and other chemicals (RMRDC, 2016).

Most common chemicals added to OBM Muds:

Barite
Bentonite
Diesel
Emulsifiers
Water

Plate VI: Unlined drilling fluid sumps were commonplace before the environmental consequences were recognized (Winter, 2017)

2.7 **Composition of Drilling Mud**

Water-based drilling mud most commonly consists of bentonite clay (gel) with additives such as barium sulphate (barite), calcium carbonate (chalk) or hematite. Various thickeners are used to influence the viscosity of the fluid, for example, xanthan gum, guar gum glycol, carboxy methylcellulose, polyanionic cellulose (PAC), or starch. In turn, de-flocculants are used to reduce viscosity of clay-based muds; anionic polyelectrolytes (for instance, acrylates, polyphosphates, lignosulphonates (Lig) or tannic acid derivates such as Quebracho) are frequently used (Cheraghian, *et al.*, 2018). Red mud was the name for a Quebracho-based mixture, named after the colour of the red tannic acid salts; it was commonly used in the 1940s to 1950s, then was made obsolete when lignosulfonates became available. Other components are added to provide various specific functional characteristics as listed. Some other common additives include lubricants, shale inhibitors, and fluid loss additives (to control loss of drilling fluids into permeable formations). A weighting agent such as barite is added to increase the overall density of the drilling fluid so that sufficient bottom hole pressure can be maintained thereby preventing an unwanted (and often dangerous) influx of formation fluids. Also, use of silica and clay nanoparticles for high pressure high temperature (HPHT) invert emulsion based muds, and observed their positive effect on the rheology of the drilling mud (Cheraghian *et al.*, 2018).

2.7.1 Factors Influencing Fluid Performance

Some factors affecting drilling fluid performance are:

- Fluids rheology
- The change of drilling fluid viscosity
- The change of drilling fluid density
- The change of mud pH

- Corrosion or fatigue of the drill string
- Thermal stability of the drilling fluid
- Differential sticking (Cheraghian *et al.,* 2018).

2.7.2 Drilling Mud Classification

They are classified based on their fluid phase, alkalinity, dispersion and the type of chemicals used.

2.7.3 Dispersed Systems

Freshwater mud: Low pH mud (7.0–9.5) that includes spud, bentonite, natural, and phosphate treated muds, organic mud and organic colloid treated mud. High pH mud example alkaline tannate treated muds are above 9.5 in pH.

Water based drilling mud that represses hydration and dispersion of clay – There are 4 types: high pH lime muds, low pH gypsum, seawater and saturated salt water muds (Winter, 2017).

2.7.4 Non-Dispersed Systems

Low solids mud: These muds contain less than 3–6% solids by volume and weight less than 9.5 lbs/gal. Most muds of this type are water-based with varying quantities of bentonite and a polymer.

Emulsions: The two types used are oil in water (oil emulsion muds) and water in oil (invert oil emulsion muds).

- Oil based mud: Oil based muds contain oil as the continuous phase and water as a contaminant, and not an element in the design of the mud. They typically contain less than 5% (by volume) water. Oil-based muds are usually a mixture of diesel fuel and asphalt however can be based on produced crude oil and mud (Duru *et al.,* 2019).

CHAPTER THREE

3.0 MATERIALS AND METHOD

The summarized list of materials and equipment used in this research work, procedure and experimental description are all stated in this section.

3.1 Materials and Equipment

Table 3.1: List of Materials and their Sources

S/N	Material	Source	Quantity
1	Barite Ore	Azara	200g
2	Oleic Acid	Kadpoly	200ml
3	Hydrochloric Acid	Kadpoly	250ml
4	Sodium Silicate	Kadpoly	200ml
5	Methyl Isobutyl Carbinol (MIBC)	Kadpoly	200ml

Table 3.2 List of Equipment

S/N	EQUIPMENT & MODEL	SOURCE
1	Hammer (WA8H)	Kad poly
2	Jaw Crusher (77DR)	Kad poly
3	Ball Mill (A162)	Kad poly
4	Jones Riffle (S12070)	Kad poly
5	Sieve Shaker (-125 to +90µm)	Kad poly
6	Pycnometer Bottle	Kad poly

3.2 Azara Barite Ore Sample Preparation for Beneficiation

The barite ore samples as received have been broken manually with sledge hammer to provide a required size acceptable to laboratory which then crushed using a Jaw crusher until the particle sizes were less than 1180µm. A Schutte Buffalo Hammer Mill (Model No: WA8H and Serial No: S1207050) and a Shambhavi Impex Ball Mill (Model No: A162. Serial No: 5R6359) were used to further reduce the particle size and achieve homogeneity in composition, then coned and quartered to yield a representative sample.

3.3 In Coning and quartering of Azara Barite Ore

Crushed material is heaped into a cone by shovelling all the material to one point on the clean table in such a manner that the particles roll down in all directions and the composition of the mass are thus distributed as concentric layers of a cone. The top of the cone is then flattened with the edge of the shovel by spreading the material equally in all directions until a disc is formed. This disc is made into quadrants and the materials from diagonally opposite quadrants are taken as sample. The material in the other quadrants are removed and rejected. The mass now contains half the original quantity. The material so sampled is then further crushed and coning and quartering are repeated, thus reducing the quantity of the sample to one fourth of its original quantity. The cycle is repeated until the sample is of the desired quantity. It was also subjected to re-sampling using a Jones Riffle and size analysis using a laboratory sieve shaker for 10mins with sieves of sizes +180µm, +90µm and pan. Samples were collected from the powder for both chemical composition analysis and concentration tests. The experiments were carried out at the Mineral Processing laboratory at the Kaduna Polytechnic Tudun Wada, Kaduna State.

3.4 Determination of Specific Gravity of Raw and Beneficiated Barite Ore

The specific gravity of the barite ore was determined before and after the beneficiation process as presented in table 3.3. This was done by washing the sample thoroughly, weighing an empty pycnometer bottle and recording the weight. The barite sample was filled into the specific gravity bottle to about one-third and re-weighed. The remaining space inside the bottle was filled with distilled water and weighed. The contents of the bottle were emptied and refilled with distilled water and the weight recorded. The specific gravity was then calculated using the formula:

SG = {Weight of Dry Mineral / Weight of Dry Mineral – Weight of Mineral in Water}

Table 3.3: Results of Specific gravity of Raw and Beneficiated Barite Ore

Parameters	Raw Sample	Beneficiated Sample
Weight of empty density bottle	23.3	23.3
Weight of empty density bottle + sample	28.3	28.3
Weight of empty density bottle + sample + Water	75.28	75.4
Weight of density bottle + water	71.6	71.6
Specific Gravity	3.787	4.166

3.5 Barite Sample Characterisation Using X-ray Fluorescence Procedure (XRF)

The chemical analysis of the barite ore was determined using X-ray Fluorescence X-MET8000. 20 g of the sample was measured with a weighing balance and loaded in the sample holder for analysis. This analysis was repeated after the froth flotation and purification processes. The phases present in the sample were determined using X-ray diffraction (Bruker D8 diffractometer) equipped with CoKα having multi-layered monochromator mirrors. The surface morphology of the samples was determined with a Phenom World Model proX Scanning Electron Microscope (SEM). The powder particles were placed on a sample holder and coated with a conducting layer of carbon and bombarded with electrons and the signals detected from the backscattered electrons were recorded.

3.6 Barite Sample Characterisation Using X-ray Diffraction Analysis Procedure (XRD)

X-ray Diffraction (XRD) pattern of barite particle were measured against utilized XRD characterization using a panlytical X'pent PRO (Neitherland) with monochromated Cuk'x radiation with scattering reflection recorded for 2Ɵ angle between 4 and 79 corresponding to d-spacing 1.34 and 3.73Å. To confirm the resolution of the diffraction peaks with standard reproducibility in 2-theta (±0.005), the sample measurement was recorded by using monochromator and dictator which were used to generate focusing beam geometry and parallel primary beam similar to that of (Abdou *et al.,* 2018). The standard diffraction data were identified according to the International Center for Diffraction Data (ICDD) software with PDF release 2011 database.

3.7 Principle and Capacities of Scanning Electron Microscopy (SEM)

The types of signals produced by a SEM include secondary electron (SE), back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence) (CL), specimen current and transmitted electrons.

Secondary electron detectors are standard equipment in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimentional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown above. A wide range of magnification is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays, because the intensity of the BSE signal is strongly related to atomic number (Z) of the specimen. BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can colloidal gold immune-labels of 5 or 10 nm diameter, which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens.

Characteristics X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher-energy electron to fill the shell and release energy. These characteristics X-rays are used to identify the composition and measure the abundance of elements in the sample (Labe *et al.*, 2018).

3.8 Sample Preparation for (SEM) Analysis

All sample must be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of SEM can examine any part of a 6-inch (15 cm) semiconductor wafer, and some can tilt an object of that size to 45^0. Samples are coated with platinum coating of electrically conducting material, deposited on the sample either by low-vacuum sputter coating or by high-vacuum evaporation. SEM instruments place the specimen in a relative high-pressure chamber where the working distance is short and the electron optical column is differentially pumped to keep vacuum adequately low at the electron gun. The high-pressure region around the sample in the ESEM neutralizes charge and provides an amplification of the secondary electron signal. Low-voltage SEM is typically conducted in an FEG-SEM because the field emission guns (FEG) is capable of producing high primary electron brightness and small spot size even at low accelerating potentials.

Embedding in a resin with further polishing to a mirror-like finish can be used for both biological and materials specimens when imaging in backscattered electrons or when doing quantitative X-rays microanalysis (Labe *et al*., 2018).

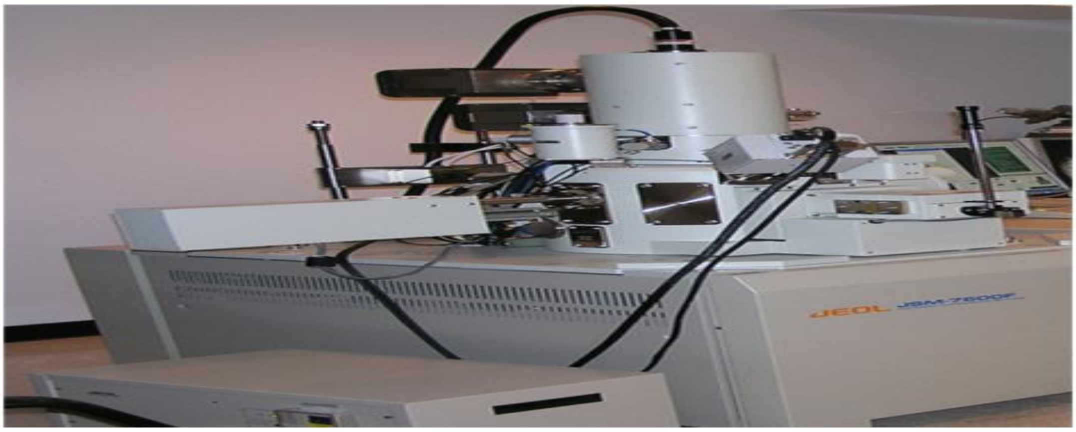


Plate VII: Picture of Scanning Electron Microscopy Machine

3.9 Methodology for the Froth Flotation / Purification of Azara Barite Ore

Two hundred grams of Azara barite sample obtained from the sieve of 125µm have been subjected to flotation experiments where 30.0% w/w solid to liquid pulp were prepared. This pulp was poured into laboratory Denver flotation cell which mixed the sample with average impeller speed of 1500rpm. About 25ml of depressant (Sodium silicate) and 50ml of collector (Oleic acid) were added to the pulp, and conditioning (without air) was done for about 10 minutes, then 20ml of frother Methyl Isobutyl Carbinol (MIBC) was added 2 minutes before the expiration of conditioning time. Air was allowed to pass through the pulp at a reasonable rate. The froths (concentrate) and (tailings) were filtered, washed and dried then weighed for further analysis as shown in Table 3.4.

Table 3.4: Result of Froth Flotation / purification of Azara Barite Ore

Particle Size	Products (Barite)		
–125μm +90μm	Feed	Concentrate	Tailing
	200g	32.02g	167.98g
	100%	16.01%	83.99%

3.10 Determination of Barite sample pH

A 20-gram sample of the sieved barite was placed in a beaker, and 20ml of distilled water was added to it. The slurry formed was allowed to stand for 70 minutes and stirred for about 10 minutes to measure the pH of the slurry (Ibe *et, al.*, 2016). The electrode remained immersed in the sample slurry until the meter stabilized. The pH was measured repeatedly after 24hrs and specifically at the temperature range of 26.3°C in line with the pH manufacturer's instruction manual (Washington State Department of Transportation (WSDT) 2009; (Ibe *et al.*, 2016).

3.11 Froth Floatation Process Diagram as Discussed in 3.2 and 3.3 Methodology

A. Raw Barite

B. Floatation of Barite

C. Dried Floated Barite

D. Concentrated Solution

Plate VIII: Pictorial Set-up of Beneficiation Process of Azara Barite Ore

3.12 Methodology of Barite Floatation (see 3.2 and 3.3 methods)

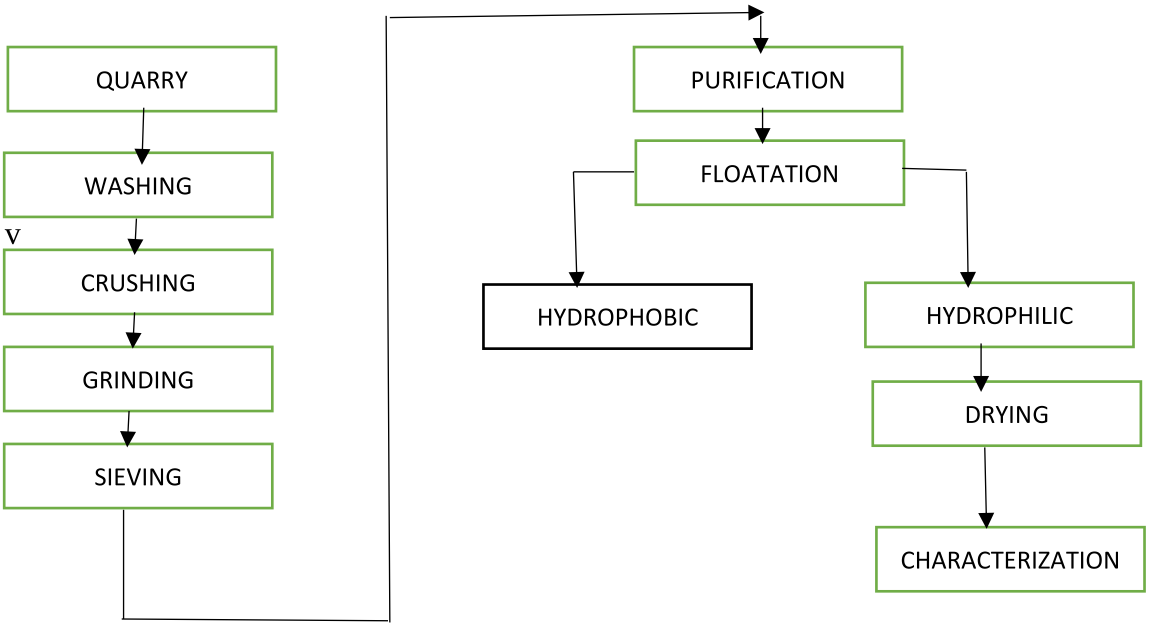


Figure 3.1: Methodology used for Beneficiation of Azara Barite Ore

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Chemical Composition Analysis Result Using X-ray Fluorescence (XRF)

Table 4.1 shows the results of the chemical composition analysis for barite sample before and after the beneficiation process at pH 7. The barite ore is associated with a lot of impurities and an analysis of the ore using X-ray Fluorescence (XRF) indicated that apart from the major elements namely; barium and sulphur, about 14 other elements were observed. The sum of all these elements amount to about 11.1%. When the amounts of Ba and S are added together, they make up about 76.3% while Fe also has a very significant quantity contributing about 10.1%. This is similar to the composition in the literature concerning Azara barite (Mgbemere *et al*., 2018). The amounts of Ba in the barite after froth floatation and purification increased to 82.1%. The amounts of the other elements decreases.

Table 4 .1: Oxide Composition of Samples using X-Ray Fluorescence (XRF) Cu-Zn

Oxide	Raw Barite	Beneficiated Barite	Tailing/Gangue
LOI	3.112	3.000	5.040
SiO2	15.411	5.350	64.020
CaO	0.443	0.085	1.121
SO3	20.042	9.061	15.247
Fe2O3	0.300	0.202	0.216
CuO	0.067	0.027	0.075
ZnO	0.043	0.003	0.008
Rb2O	0.002	< LOD	< LOD
SrO	0.438	0.110	0.863
ZrO2	0.008	< LOD	0.002
Eu2O3	0.081	< LOD	< LOD
BaO	56.224	82.116	13.403
Re2O7	0.002	< LOD	0.004
PbO	< LOD	< LOD	< LOD
Total	99.999	99.999	99.999

LOD: Low Detection

Table 4.2: XRF Analysis of Imported Barite Ore (Abdou *et, al.* 2018)

Element	Barite ($BaSO_4$)	SiO_2	MgO	Fe_2O_3	L.O.I
Beneficiated Result (%)	94.5	2	0.5	0.5	2.5
Raw Result (%)	67.5	25.5	1.5	2.5	3.0

4.2 XRF Analysis Chart for Azara Barite Ore

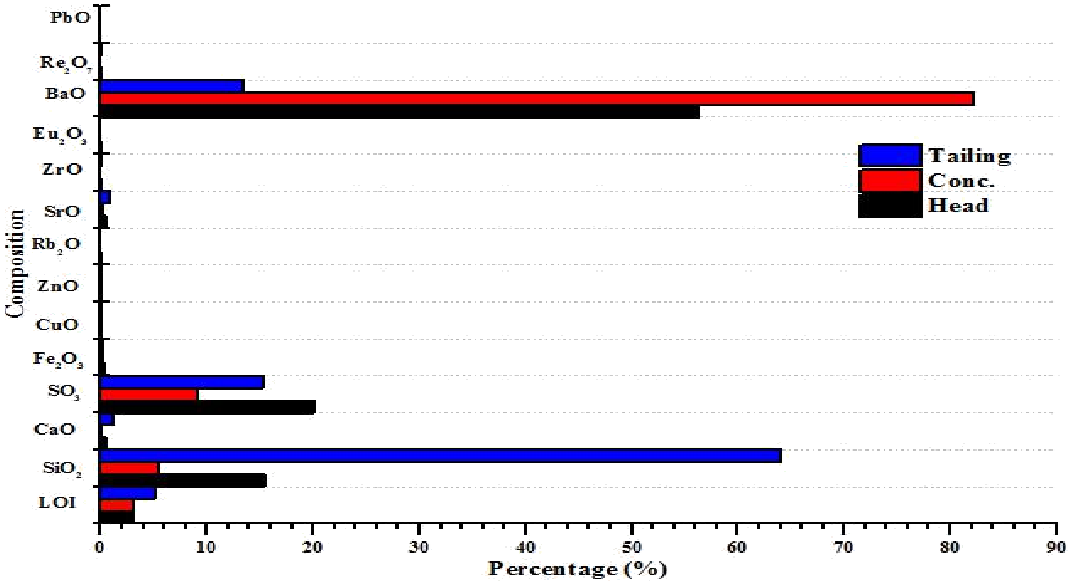


Figure 4.1: Percentage Concentration of a various Component of Barite Ore before and after Beneficiation

Concentration of constituents in barite ore was analysed using XRF as indicated in figure 4.1 above based on their percentages, with BaO 82.1% which is the highest follow by impurities after beneficiation process completed. This shows characterisation with X-ray Fluorescence has achieve required result.

The elemental composition of raw barite ore has more impurities compared to when its finally beneficiated is shown above, this means a lot of work has been done to Azara barite ore to improve its percentage purity from 56.2% and above in order to be use

The chart shows that the barite ore has been beneficiated with composition of Barium Oxide 82.1% as identify using X-ray Fluorescence. Characterized component is subjected to further purification to determine it compatibility as component of drilling fluid. Average purity have been meet if going by the standard value range of at least

80.0% and above. Impurities of the barite ores which is refer to tailing as shown above, were successfully eliminated by the use of froth flotation technique as characterized by XRF resulting to SiO 64.0%, SO$_3$ 15.2%, and LOI 5.0% etc.

4.3 Purification and froth flotation Result of Azara Barite Ore

The result of the froth flotation process that was carried out on the Azara barite is shown in Table 4.3. The froth and depressed minerals are the products from froth flotation operations. The froth contains the desired mineral while the depressed mineral contains both the impurities and some of the desired minerals. As the pH of the flotation process increases, the amount of froth obtained increases while the depressed minerals decrease. At a pH of 5, 7 and 9, the amount of froth recovered are 65.8%, 67.2% and 70.7% respectively similar to that reported by (Mgbemere *et, al.,* 2018). The amounts of the depressed minerals are 32.4%, 31.6% and 28.3% respectively. The remaining amounts are lost during the froth flotation experiment. The chemical composition analysis was carried out only on the sample with pH of 7. The amount of impurity elements present in the barite is still high with the percentage of the impurities marginally increasing to 5.23. The amount of sulphur slightly decreases to 9.1% while that of barium increases to 82.1%. The concentration of barium in the froth at different pH values indicate that 81.8% was obtained at a pH of 5, 82.1% at pH of 7 and 79.9 at a pH of 9. The S.G values have been obtained at pH values of 5, 7 and 9 corresponding to S.G. values of 3.787±0.017, 4.166±0.026 and 4.054±0.01 respectively.

Table 4.3: Purification and Froth Flotation of Barite Ore at Different pH Value

S/NO	Ph	Weight of Froth (g)	Weight of Depressed (g)	Loss
1	5	197.43	97.2	5.44
2	7	201.74	94.64	3.64
3	9	212.22	85	2.80

4.4 X-ray Diffraction (XRD) Analysis of Raw and Beneficiated Azara Barite Ore

The phase purity and crystalline of the pure $BaSO_4$ both raw and beneficiated were examined by X-ray diffraction technique (XRD) (figure 4.2). the crystal structure of $BaSO_4$ is orthorhombic dipyramidal with space group Pnma and lattice parameters a = 8.884(2) Å b = 5.457(3) Å and c = 7.157(2) Å. the values match precisely with standard data (ICCD card No. 41 – 1445). All XRD patterns reflect the existence of pure barium sulphate peaks; however, new peaks emerged in the composition architectures evidencing presence of quartz, Fe_2SO_3 and SiO_2. molecular concentrations. A new peak (004) is observed at 2θ, 36.48° in the $BaSO_4$, the intensity of which increased systematically with increasing component concentration i.e from 0.1M to 0.5M. However, at high concentration rutile phase also occurred as evidenced from the crystalline peaks of each sample respectively as shown in (Figure 4.2 – 4.5).

X-ray diffraction patterns for Azara raw barite ore shows a fitting of the raw barite ore with reference pattern (barite) in the database to contains about 75% $BaSO_4$. The analysis also indicates that in addition to the barite present, other minerals like SiO_2 and Fe_2O_3 are also present which required purification to obtained valuable mineral to be use in drilling fluid. The characteristic peaks however correspond to that of imported barite shown in (figure 4.3 and 4.5) with X-ray diffraction pattern the same although the impurities vary.

4.5 XRD Diffractograms/Patterns of Barite Ore

The figures below are the patterns of XRD for raw and beneficiated barite ore.

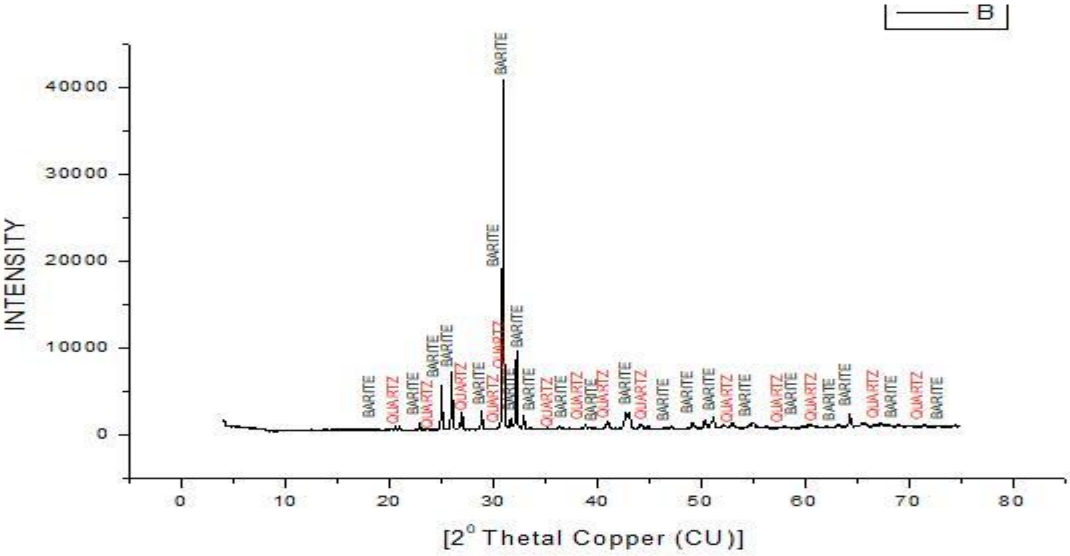


Figure 4.2: X-ray Diffraction of Raw Barite Ore

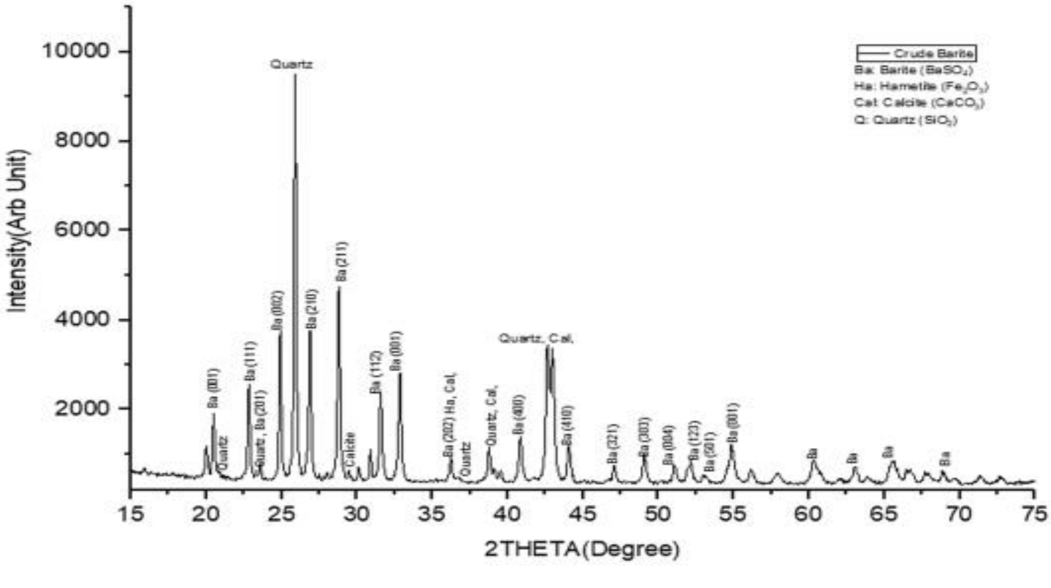


Figure 4.3: X-ray Diffraction of Raw Imported Barite Ore.

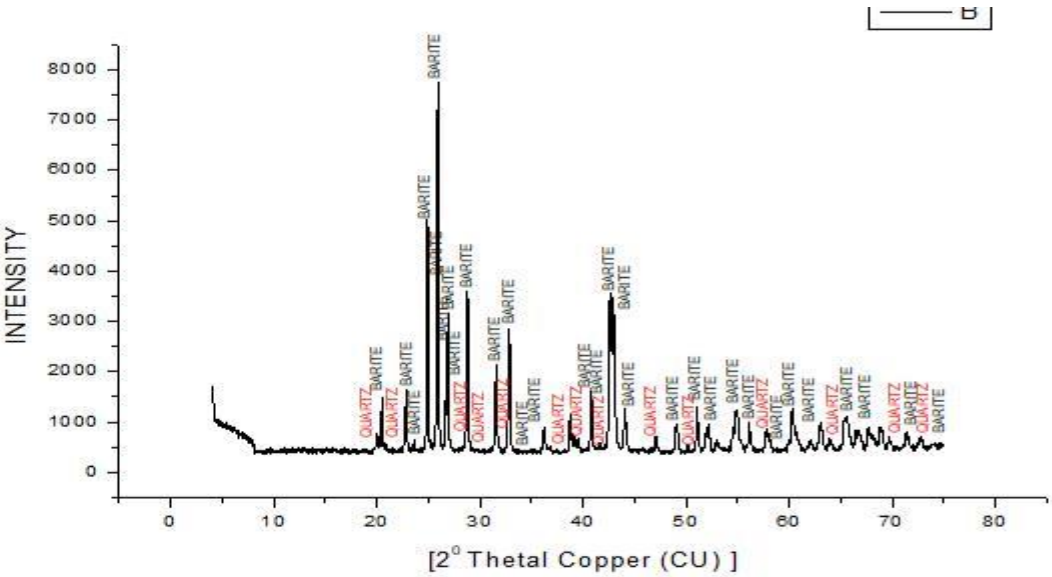


Figure: 4.4: X-ray Diffraction of Beneficiated Barite Ore

After the froth flotation process, the diffraction peaks become very sharp indicating that the crystallinity of the sample has been enhanced. The diffraction pattern after beneficiation was also analysed with the reference from the database for barite (96–900–4123) and found to contain about 83.99% barite as shown in (figure 4.4 and 4.5) above as its correspond to figure 4.8 of imported beneficiated b arite with similar characteristic peaks.

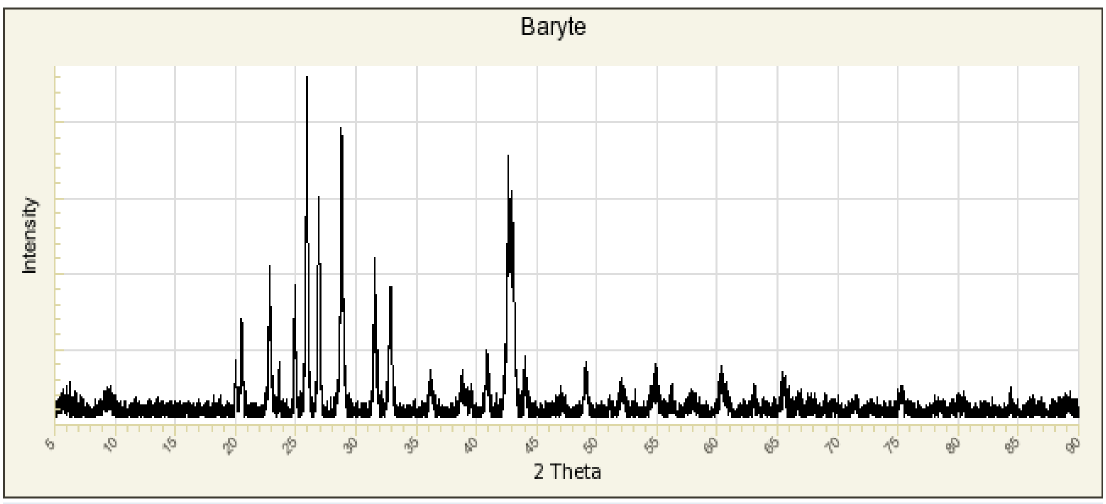


Figure 4.5: X-ray Diffraction of Beneficiated Imported Barite Ore

4.6 Scanning Electron Microscopy (SEM) of Azara Barite Ore

The scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis of morphology and element percentage composition data are shown in (Figures 4.6 to 4.9). The morphology of sample Azara / Wuse barite, showed surfaces of barite embedded form of material structure with clear unit boundaries in (figure 4.6 and 4.7) for beneficiated and raw barite ore at different magnifications. The working imported barite sample showed a fine surface in the morphology monograph. The surface chemical analysis was carried out with EDX, revealing the different elemental compositions of the material in-depth surfaces (Table 4.4). Sample of the ore revealed a composition of Ba as 50.81%, S as 8.1%, and Fe as 19.8%, Si as 7.3%, Nb as1.9% etc. This gave 100% of the Ba-S-O empirical composition. Sample imported barite showed a composition of Ba as 52.3%, S as 25.9%, and oxygen as 16.4%. This gave 94.5% of the Ba-S-O empirical composition. The imported sample showed a much lower element composition empirical percentage indicating that most of the samples will be suitable for drilling fluid purposes. No significant change could be observed on the microstructures of both samples. However, large and small grains with significant pores could be observed which indicate various distributions of elements in Azara barite ore.

The pure $BaSO_4$ demonstrate a porous morphology, the composition post treatment systematically filled the pores in the nano-particle surface as seen in (figure 4.6), thereby making a $BaSO_4$ nanowire. Although the effect is not clear for raw Azara barite concentration treatment, particularly at the surface of nano-particles, the beneficiated Azara barite systematically developed nano-particle (size 5 – 10nm) which is not only formed a thin BaO over layer but filled with gaps between adjacent Fe resulting in improved interconnectivity of the grains composition.

Although porosity of the photoanode materials favours electrolyte penetration and enhanced BaO intake, it increases grain boundary density and reduce particle-particle interconnectivity thereby resulting in high charge transport resistance. Fe, Mn, O, Ti and Se served as a medium to fill the void in pure $BaSO_4$ (figure 4.6 and 4.7) which is expected to increase the transport properties of the photoanode film. Cross-sectional view of the photoanode films demonstrated the presence of multiple pores (pores diameter 30nm) in pure $BaSO_4$ in (figure 4.6).

Table: 4.4: Scanning Electron Microscopy EDX Barite Data

Element Number	Element Symbol	Element Name	Atomic Concentration	Weight Concentration
56	Ba	Barium	24.24	50.81
26	Fe	Iron	23.27	19.83
16	S	Sulphur	16.54	8.10
14	Si	Silicon	16.96	7.27
41	Nb	Niobium	1.35	1.92
47	Ag	Silver	1.14	1.88
25	Mn	Manganese	1.73	1.45
19	K	Potassium	2.23	1.33
20	Ca	Calcium	1.79	1.09
17	Cl	Chlorine	1.71	0.92
23	V	Vanadium	0.90	0.70
11	Na	Sodium	1.39	0.49
12	Mg	Magnesium	0.92	0.34
15	P	Phosphorus	0.53	0.25
22	Ti	Titanium	0.00	0.00
16	O	Oxygen	15.96	32.06

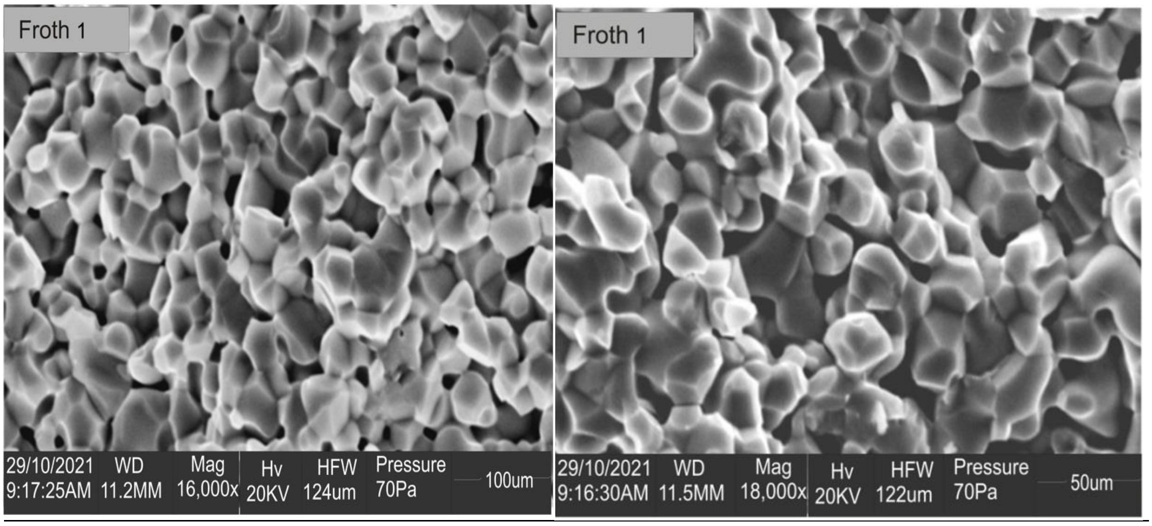


Figure: 4.6: Scanning Electron Microscopy of Azara Barite Ore after Beneficiation

In SEM images above shows beneficiated barite ore with pores based on the grain sizes presence as magnification increases 16,000x, 100µm and 18,000x, 50µm respectively. However, there is no significant difference between the microstructures in the images.

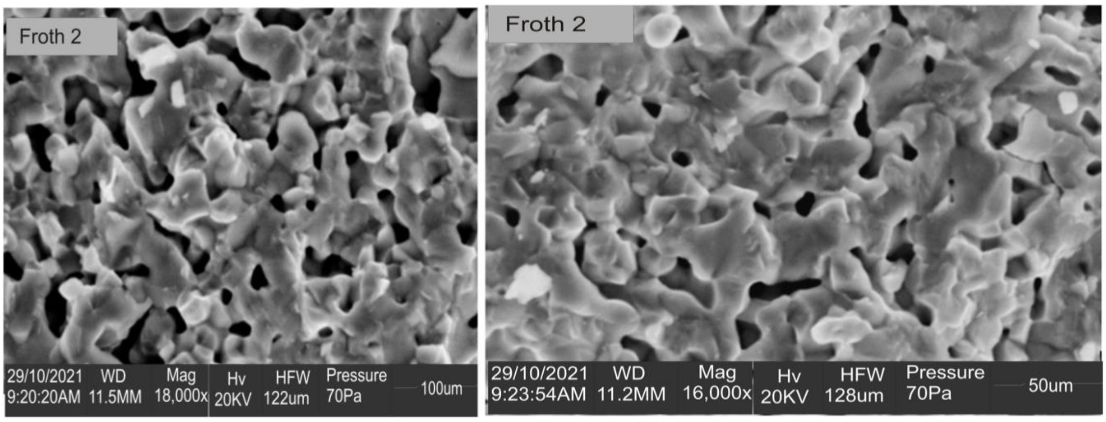


Figure: 4.7: Scanning Electron Microscopy of Azara Barite Ore before Beneficiation

The SEM images in (figure 4.7) above shows that the reaction between components presence in raw barite ore which indicate the need to beneficiate the ore. However, impurities in the barite ore shows the nature of micro-sized particles used in this beneficiation process with magnifications 18,000x, 100µm and 16,000x, 50µm for the raw Azara barite ore full of impurities.

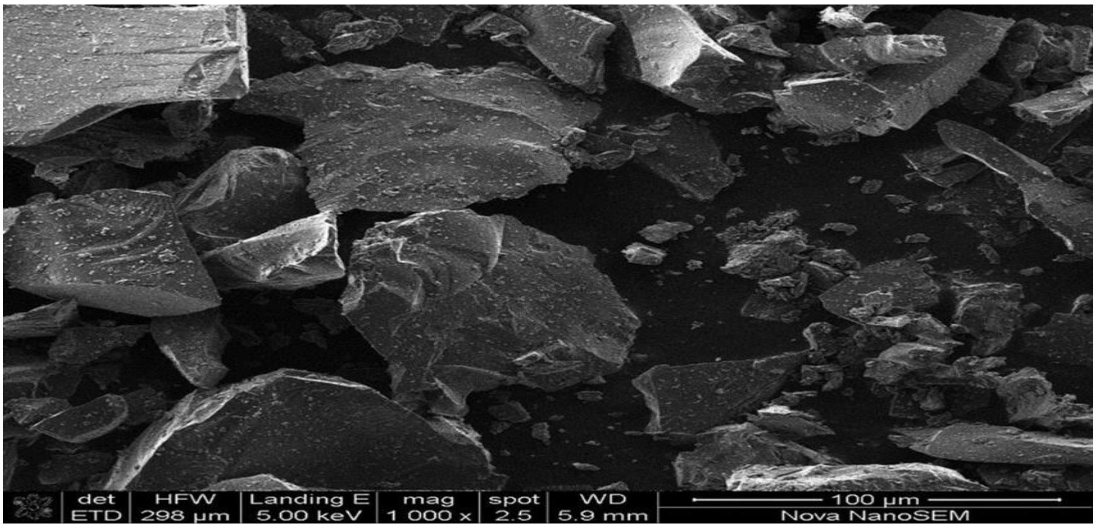


Figure: 4.8: Scanning Electron Microscopy Raw Imported Barite

SEM micrographs of micro-sized raw imported barite particle illustrated above. This clearly shows the realistic nature of the micro-sized particles to be use in this study as reference (Abdou *et, al.* 2018). This characteristic image revealed that, barite particles have a Platy-shaped morphology as shown which give an idea about the reaction mechanism of these particles as a viscosifier in formulation of drilling fluid.

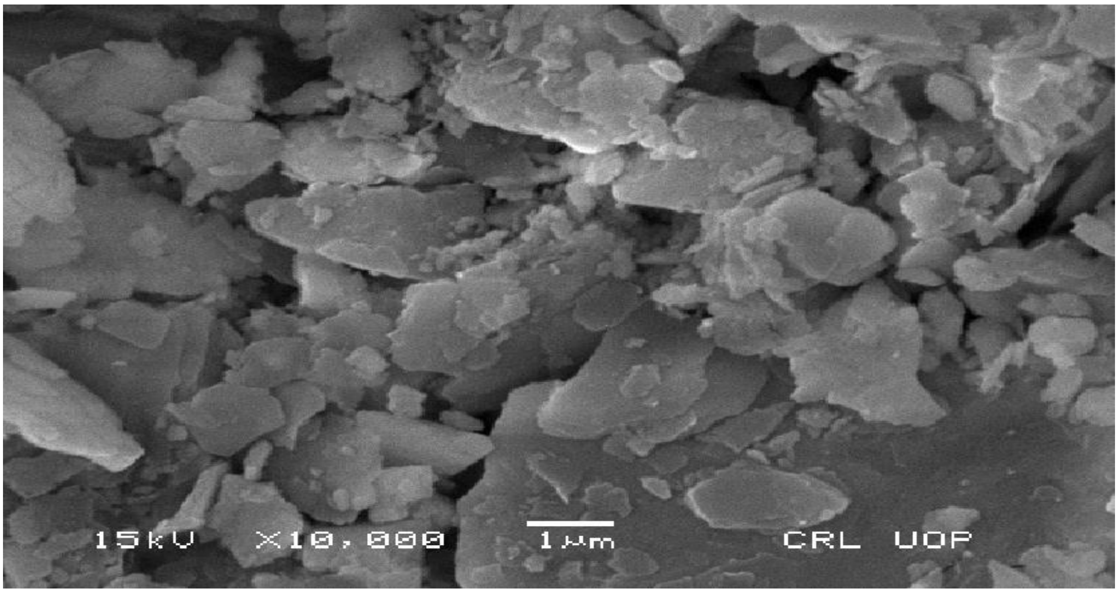
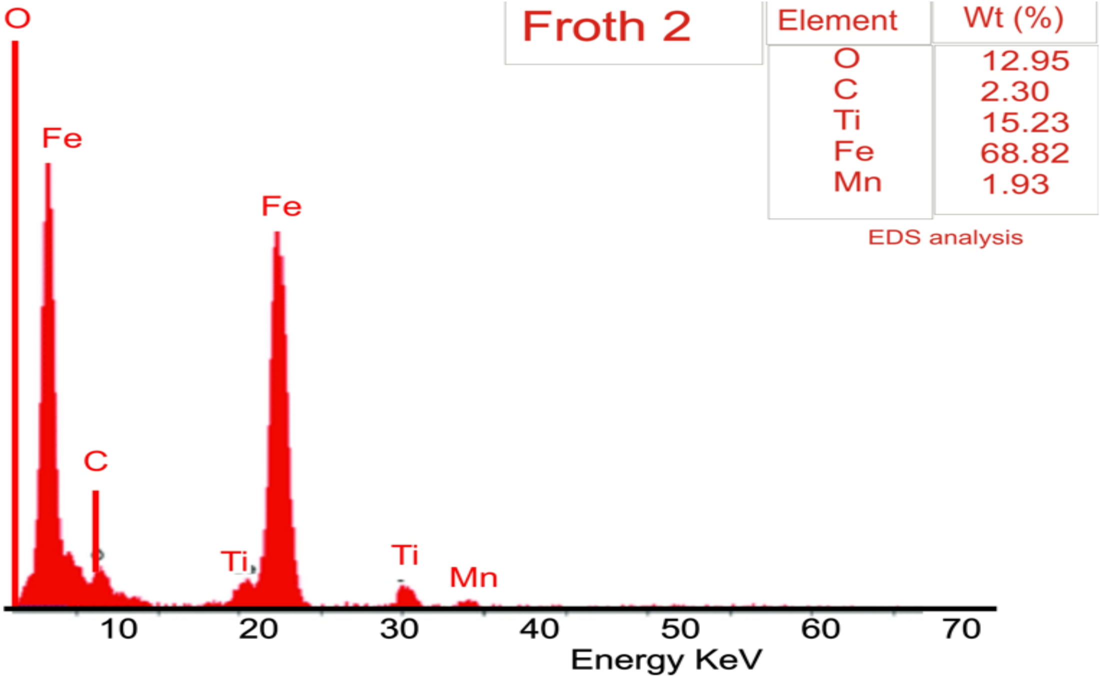


Figure: 4.9: Scanning Electron Microscopy Beneficiated Imported Barite

The SEM image illustrated in (Figure 4.9) shows fragments of micro-sized barite particles with square, angular and sub-angular shape that support its utilization to be use as weighting agent in drilling fluid technology. The morphology of barite particles supports its utilization for enhancing the weighting properties of drilling fluids. The diameter of these particles shown from SEM images is 1µm size.

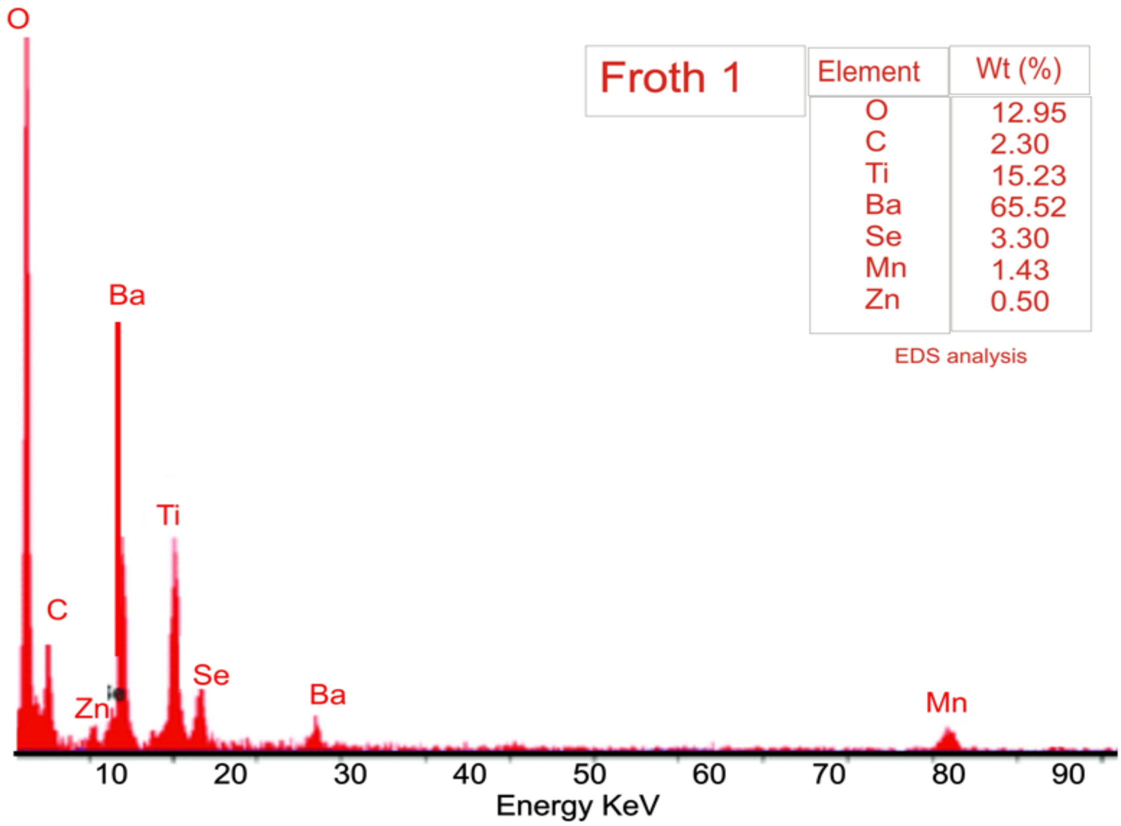
4.7 SEM EDX of Azara Barite Ore



Element	Wt (%)
O	12.95
C	2.30
Ti	15.23
Fe	68.82
Mn	1.93

Figure 4.10: Scanning Electron Microscopy EDX of Raw Azara Barite Ore showing distribution of elements

The raw Azara barite ore EDX came with a lot of impurities, the element composition presence where oxygen 12.9%, carbon 2.3%, Tin 15.2% Iron 68.8% and Manganese to contain 1.9% as shown in (Figure 4.10) above with Fe form the highest component.



Froth 1

Element	Wt (%)
O	12.95
C	2.30
Ti	15.23
Ba	65.52
Se	3.30
Mn	1.43
Zn	0.50

EDS analysis

Figure: 4.11: Scanning Electron Microscopy EDX of Beneficiated Azara Barite Ore showing distribution of elements

In order to confirm the formation of barite ($BaSO_4$) composition EDX analysis was performed on beneficiated Azara barite ore. During the EDX measurement different area were focused and the corresponding peaks are shown in (figure 4.11) above, to have contain O 12.9%, C 2.3%, Sn 15.2%, Ba 65.5%, Se 3.3%, Mn 1.4%, and Zn 0.5% as seen in synthesis nanostructure in EDX spectrum. Details of EDX spectra of the electrospun of $BaSO_4$ value measured in atomic and weight % from the graph.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

To assess the suitability of barite ore for drilling fluid/mud the use of froth flotation and purification process are used to increase the concentration of both $BaSO_4$ found in barite ore from Azara in Nassarawa State Nigeria. It is clear that using only one beneficiation method may not be very effective in removing as many impurities as is necessary to obtain an industrially acceptable specific gravity value. The pH of a solution is a very important parameter in the processing of barite as the floated sample with pH of 7.0 will always give the highest specific gravity values. The X-ray diffraction data reveals that the diffraction pattern shows crystallisation of barite at different peaks while the chemical analysis indicates the formation of complex oxides.

The purification in beneficiation processes resulted in a high specific gravity value with crystalline diffraction peaks and chemical composition resulted in little impurity elements as possible. Comparison of the analytical and characterization results reported for standard Barite with those obtained from the purified Azara Barite using equipment such as, XRF, XRD, SEM-EDX and particularly its Specific gravity (4.2 obtained for purified Azara Barite compare favourably with 4.2-5 reported for standard Barite). Specific gravity determines suitability of purified/standard Barite for the production of drilling fluid. From this comparison of the characterization and analytical results obtained from the purified Azara Barite with those reported for standard Barite, it was observed and can be seen clearly that they were in a very close agreement. Therefore, beneficiated and purified Azara-Barite concentrates obtained using Froth flotation-beneficiation method from raw/crude Azara

Barite ore mined in Nasarawa State, Nigeria has a greater potential to replace imported (Standard) Barite used in the production of drilling fluid when given required attention.

5.2 Recommendations

1. Use of barite for other industrial applications including healthcare, construction, plastic, cosmetics, paper, and rubber industries due to their level of barium content in the range of 50 to 80% should be encourage.
2. The metallic content such as Ca, Pb, Zn, Mg, Cu, and Cd minerals, and extractable carbonates in Azara barite was within the limits set by the American Petroleum Institute (API) and Nigerian Department of Petroleum Resources (DPR). However, the quantity of iron mineral in Azara barite is higher than the API set limits but low when compared with the DPR set limit, Azara barite can replace imported ones to be use in drilling fluid.
3. Nigeria government should consider setting up barite processing plants across the country and maintain the existing ones in the country.

5.3 Contribution to Knowledge

- In this research work, raw Azara barite was successfully processed and purified into an industrial grade barite with the aid of froth flotation method.
- Comparison between Azara raw barite and imported barite have been established, Azara barite was found to be efficient in percentage purity and has potential to replace imported barite.
- The research has also reveal more impurities was successfully removed from Azara barite to obtained pure barite to be use as drilling fluid in Nigeria oil & gas.

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APPENDIX A

Dataset Name: RAW BARITE XRD DATA

File name: C:\Users\USER\Desktop\DOCS\2020\10\MUAZU\MUAZU RAW.xrdml

JARA

Sample Identification:

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0.0001; Minimum step size Omega: 0.0001

Sample stage = Reflection-transmission spinner; Minimum

step size Phi: 0.1

Diffractometer system = EMPYREAN

Measurement program = NGRL Absolute Programme, Owner

= User-1, Creation date = 1/27/2017 12:19:54 PM

Official NGSA Programme

10/09/2020 15:49:25

Measurement Date / Time:

Operator: U

Raw Data Origin: XRD measurement (*.XRDML)

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End Position [°2Th.]: 74.9845

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Scan Step Time [s]: 23.9700

Scan Type: Continous

SD Mode: Scanning

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Offset [°2Th.]: 0.0000

Divergence Slit Type: Automatic

Irradiated Length [mm]: 10.00

Specimen Length [mm]: 10.00

Measurement Temperature [°C]: 25.00

Anode Material: Cu

K-Alpha1 [Å]: 1.54060

K-Alpha2 [Å]: 1.54443

K-Beta [Å]: 1.39225

K-A2 / K-A1 Ratio: 0.50000

Generator Settings: 40 mA, 45 kV

Diffractometer Type: 0000000011078671

Diffractometer Number: 0

Goniometer Radius [mm]: 240.00

Dist. Focus-Diverg. Slit [mm]: 100.00

Incident Beam Monochromator: No

Spinning: Yes

Peak List

[redacted]

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8.0124	103.04	0.2558	11.03477	0.26
20.1123	162.20	0.1535	4.41510	0.41
20.5399	417.21	0.1023	4.32415	1.05
20.9368	432.99	0.1023	4.24307	1.09
22.8936	735.04	0.1279	3.88463	1.85
24.9976	5251.34	0.1279	3.56223	13.20
25.9789	6507.29	0.1279	3.42987	16.36
26.6985	835.32	0.0768	3.33903	2.10
26.9607	1971.53	0.1279	3.30716	4.96
28.8660	2157.95	0.1279	3.09306	5.42
30.9086	39783.38	0.1535	2.89315	100.00
31.6465	1211.21	0.1535	2.82736	3.04
32.2095	8777.90	0.1279	2.77921	22.06
32.8824	1549.98	0.1279	2.72386	3.90
36.3208	304.29	0.1791	2.47350	0.76
37.3755	120.13	0.1535	2.40609	0.30
38.8105	515.60	0.1535	2.32037	1.30
39.2323	219.67	0.1535	2.29639	0.55
40.8891	799.60	0.0768	2.20708	2.01
42.6925	1904.31	0.1535	2.11794	4.79

43.0066	1933.77	0.0936	2.10146	4.86
43.1254	1552.62	0.0768	2.09768	3.90
44.1671	544.49	0.1535	2.05059	1.37
44.8733	319.62	0.1023	2.01995	0.80
47.1529	200.17	0.2558	1.92748	0.50
49.1135	545.18	0.2047	1.85502	1.37
50.3396	884.82	0.1279	1.81268	2.22
51.1896	1274.90	0.0768	1.78456	3.20
52.2393	377.43	0.2047	1.75115	0.95
53.0260	507.02	0.3070	1.72701	1.27
54.9374	657.96	0.1535	1.67136	1.65
56.2437	298.05	0.2047	1.63560	0.75
57.9753	190.24	0.4093	1.59080	0.48
60.4087	427.24	0.2814	1.53242	1.07
63.2812	383.77	0.4093	1.46960	0.96
64.2967	1483.92	0.1248	1.44762	3.73
64.5031	767.04	0.0936	1.44707	1.93
65.7143	558.14	0.2496	1.41978	1.40
67.2933	519.00	0.1248	1.39026	1.30
68.8802	299.02	0.3120	1.36205	0.75
71.4981	258.50	0.3120	1.31847	0.65
72.8158	126.84	0.4992	1.29783	0.32

Pattern List

[redacted]

Visible	Ref.Code	Score	Compound Name	Displ.[°2Th]	Scale Fac.	Chem. Formula
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*	96-900-1420	14	Dolomite	0.000	0.021	Ca3.00 Mg3.00 C6.0...
*	96-900-4123	37	Barite	0.000	0.024	Ba4.00 S4.00 O16.00

APPENDIX B

Dataset Name:

File name:

Scan Type:

PSD Mode:

Sample Identification:

Comment:

Measurement Date / Time:

Operator:

Raw Data Origin:

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Start Position [°2Th.]:

End Position [°2Th.]:

Step Size [°2Th.]:

Scan Step Time [s]:

CONCENTRATED BARITE XRD DATA

C:\Users\USER\Desktop\DOCS\2020\10\MUAZU\MUAZU

CONCENTRATED.xrdml

IHUGH

Configuration=Reflection-transmission Spinner Stage,

Owner=User-1, Creation date=7/27/2010 10:30:07 AM

Goniometer=Theta/Theta; Minimum step size 2Theta:0.0001;

Minimum step size Omega: 0.0001

Sample stage = Reflection-transmission spinner; Minimum

step size Phi: 0.1

Diffractometer system = EMPYREAN

Measurement program = NGRL Absolute Programme,

Owner=User-1, Creation date=1/27/2017 12:19:54 PM

Official NGSA Programme

11/09/2020 11:26:27

U

XRD measurement (*.XRDML)

Gonio

4.0045

74.9845

0.0260

23.9700

Continuous

Scanning

PSD Length [°2Th.]: 3.35

Offset [°2Th.]: 0.0000

Divergence Slit Type: Automatic

Irradiated Length [mm]: 10.00

Specimen Length [mm]: 10.00

Measurement Temperature [°C]: 25.00

Anode Material: Cu

K-Alpha1 [Å]: 1.54060

K-Alpha2 [Å]: 1.54443

K-Beta [Å]: 1.39225

K-A2 / K-A1 Ratio: 0.50000

Generator Settings: 40 mA, 45 kV

Diffractometer Type: 0000000011078671

Diffractometer Number: 0

Goniometer Radius [mm]: 240.00

Dist. Focus-Diverg. Slit [mm]: 100.00

Incident Beam Monochromator: No

Spinning: Yes

Peak List

[redacted]

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20.0061	339.74	0.1279	4.43831	4.82
20.4948	1025.25	0.1023	4.33356	14.55
22.8464	1157.70	0.1279	3.89256	16.43
23.6219	236.23	0.1279	3.76648	3.35
24.9256	4512.78	0.1023	3.57236	64.04
25.9070	7046.65	0.1279	3.43922	100.00
26.6682	939.22	0.0768	3.34276	13.33
26.8933	2700.50	0.1279	3.31529	38.32
28.8025	3046.68	0.1535	3.09973	43.24
31.5781	1671.48	0.1535	2.83332	23.72
32.8435	2470.08	0.1535	2.72700	35.05
36.2303	465.37	0.1279	2.47947	6.60
38.7493	686.84	0.1023	2.32389	9.75
39.1055	315.14	0.1535	2.30354	4.47
39.5370	232.53	0.1535	2.27939	3.30
40.8308	1194.08	0.1279	2.21010	16.95
41.6573	174.56	0.2047	2.16814	2.48
42.6254	3048.29	0.1791	2.12112	43.26
42.9495	3034.58	0.2047	2.10586	43.06
44.0595	773.74	0.1279	2.05535	10.98
47.0622	292.76	0.1023	1.93098	4.15
49.0533	528.80	0.2047	1.85716	7.50
50.2199	68.93	0.2558	1.81672	0.98
51.0600	877.83	0.0768	1.78878	12.46

52.1655	516.51	0.1279	1.75345	7.33
53.0112	214.33	0.2047	1.72745	3.04
54.5282	462.85	0.0768	1.68293	6.57
54.8487	775.21	0.1279	1.67385	11.00
56.1454	534.43	0.0768	1.63823	7.58
57.8081	421.62	0.1023	1.59501	5.98
60.2998	786.16	0.1535	1.53492	11.16
62.0496	178.45	0.3070	1.49578	2.53
63.0435	547.34	0.1535	1.47457	7.77
65.3501	581.89	0.1560	1.42681	8.26
65.6742	645.54	0.1535	1.42173	9.16
66.6124	285.28	0.6140	1.40397	4.05
67.6615	407.24	0.1535	1.38473	5.78
68.8119	425.11	0.1023	1.36436	6.03
69.6880	205.02	0.2047	1.34934	2.91
71.3885	284.40	0.1535	1.32132	4.04
72.7559	203.16	0.2558	1.29982	2.88

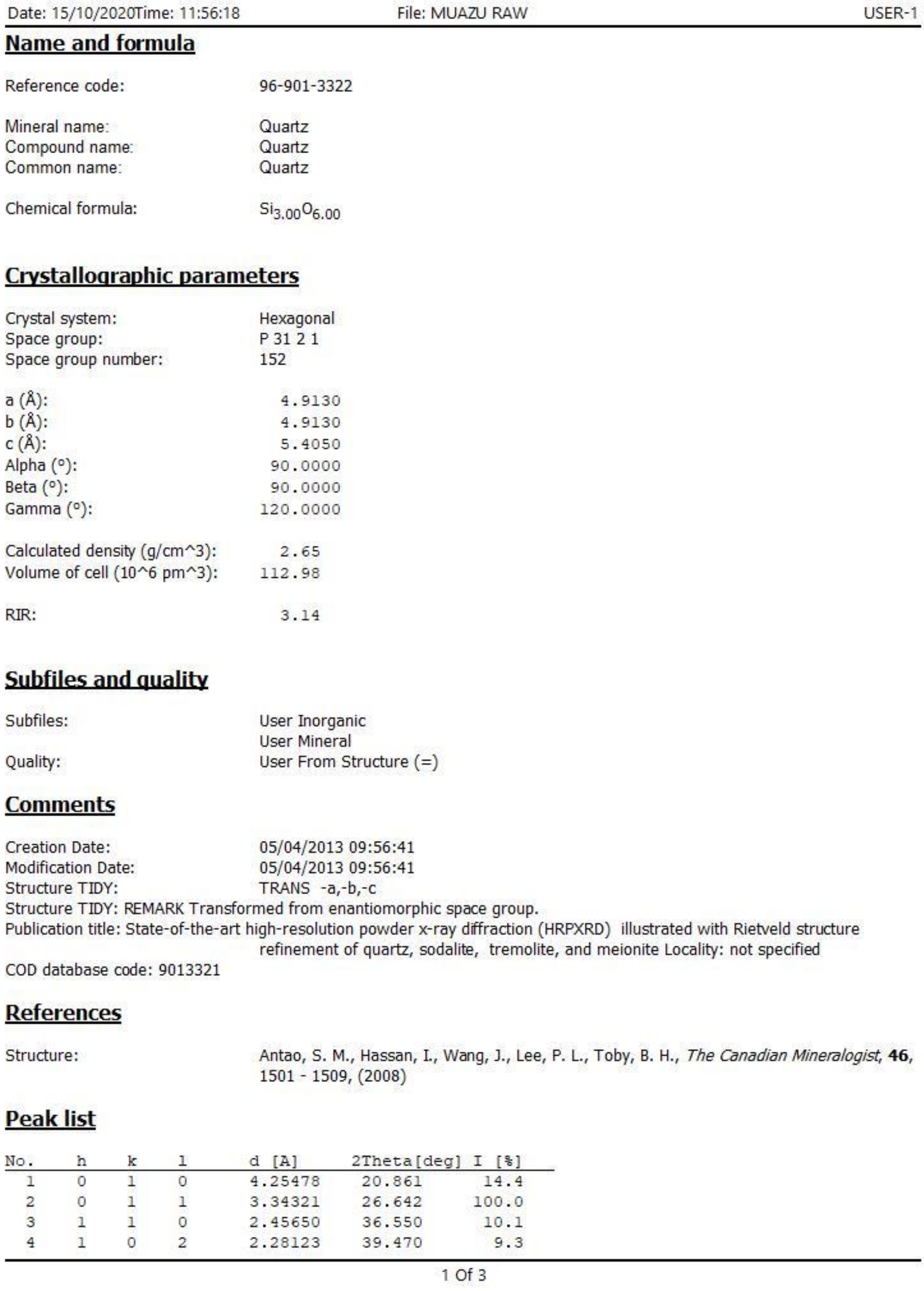
Pattern List

[redacted]

Visible	Ref.Code	Score	Compound Name	Displ.[°2Th]	Scale Fac.	Chem. Formula
*	96-900-4486	83	Barite	0.000	0.428	Ba4.00 S4.00 O16.00
*	96-900-5018	22	Quartz	0.000	0.094	Si6.00 O6.00

APPENDIX C

XRD RESULT OF RAW QUARTZ



Date: 15/10/2020Time: 11:56:18 File: MUAZU RAW USER-1

Name and formula

Reference code:	96-901-3322
Mineral name:	Quartz
Compound name:	Quartz
Common name:	Quartz
Chemical formula:	$Si_{3.00}O_{6.00}$

Crystallographic parameters

Crystal system:	Hexagonal
Space group:	P 31 2 1
Space group number:	152
a (Å):	4.9130
b (Å):	4.9130
c (Å):	5.4050
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	120.0000
Calculated density (g/cm^3):	2.65
Volume of cell (10^6 pm^3):	112.98
RIR:	3.14

Subfiles and quality

Subfiles:	User Inorganic User Mineral
Quality:	User From Structure (=)

Comments

Creation Date: 05/04/2013 09:56:41
Modification Date: 05/04/2013 09:56:41
Structure TIDY: TRANS -a,-b,-c
Structure TIDY: REMARK Transformed from enantiomorphic space group.
Publication title: State-of-the-art high-resolution powder x-ray diffraction (HRPXRD) illustrated with Rietveld structure refinement of quartz, sodalite, tremolite, and meionite Locality: not specified
COD database code: 9013321

References

Structure: Antao, S. M., Hassan, I., Wang, J., Lee, P. L., Toby, B. H., *The Canadian Mineralogist*, **46**, 1501 - 1509, (2008)

Peak list

```
No.    h    k    l      d [A]     2Theta[deg] I [%]
  1    0    1    0    4.25478     20.861      14.4
  2    0    1    1    3.34321     26.642     100.0
  3    1    1    0    2.45650     36.550      10.1
  4    1    0    2    2.28123     39.470       9.3
```

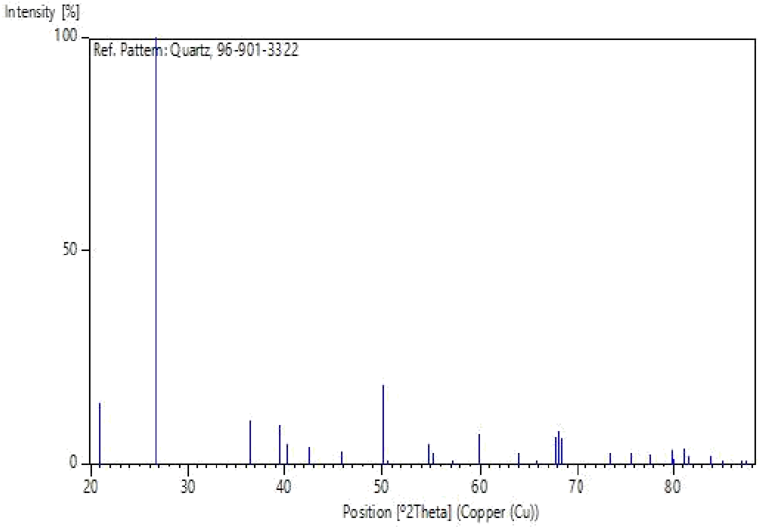
1 Of 3

5	1	1	1	2.23636	40.296	4.8
6	0	2	0	2.12739	42.457	3.9
7	2	0	1	1.97957	45.800	3.0
8	1	1	2	1.81777	50.145	18.4
9	0	0	3	1.80167	50.624	0.5
10	0	2	2	1.67160	54.879	4.5
11	0	1	3	1.65906	55.330	2.5
12	2	1	0	1.60816	57.240	0.2
13	1	2	1	1.54138	59.967	7.3
14	1	1	3	1.45281	64.040	2.6
15	3	0	0	1.41826	65.794	0.3
16	1	2	2	1.38198	67.751	6.3
17	2	0	3	1.37487	68.149	7.9
18	0	3	1	1.37182	68.322	6.2
19	1	0	4	1.28786	73.471	2.6
20	3	0	2	1.25583	75.668	2.8
21	2	2	0	1.22825	77.681	2.2
22	2	1	3	1.19974	79.890	3.5
23	2	2	1	1.19771	80.053	1.2
24	1	1	4	1.18395	81.176	3.7
25	1	3	0	1.18006	81.500	2.1
26	1	3	1	1.15291	83.847	2.1
27	2	0	4	1.14062	84.961	0.4
28	2	2	2	1.11818	87.084	0.0
29	3	0	3	1.11440	87.454	0.4

Structure

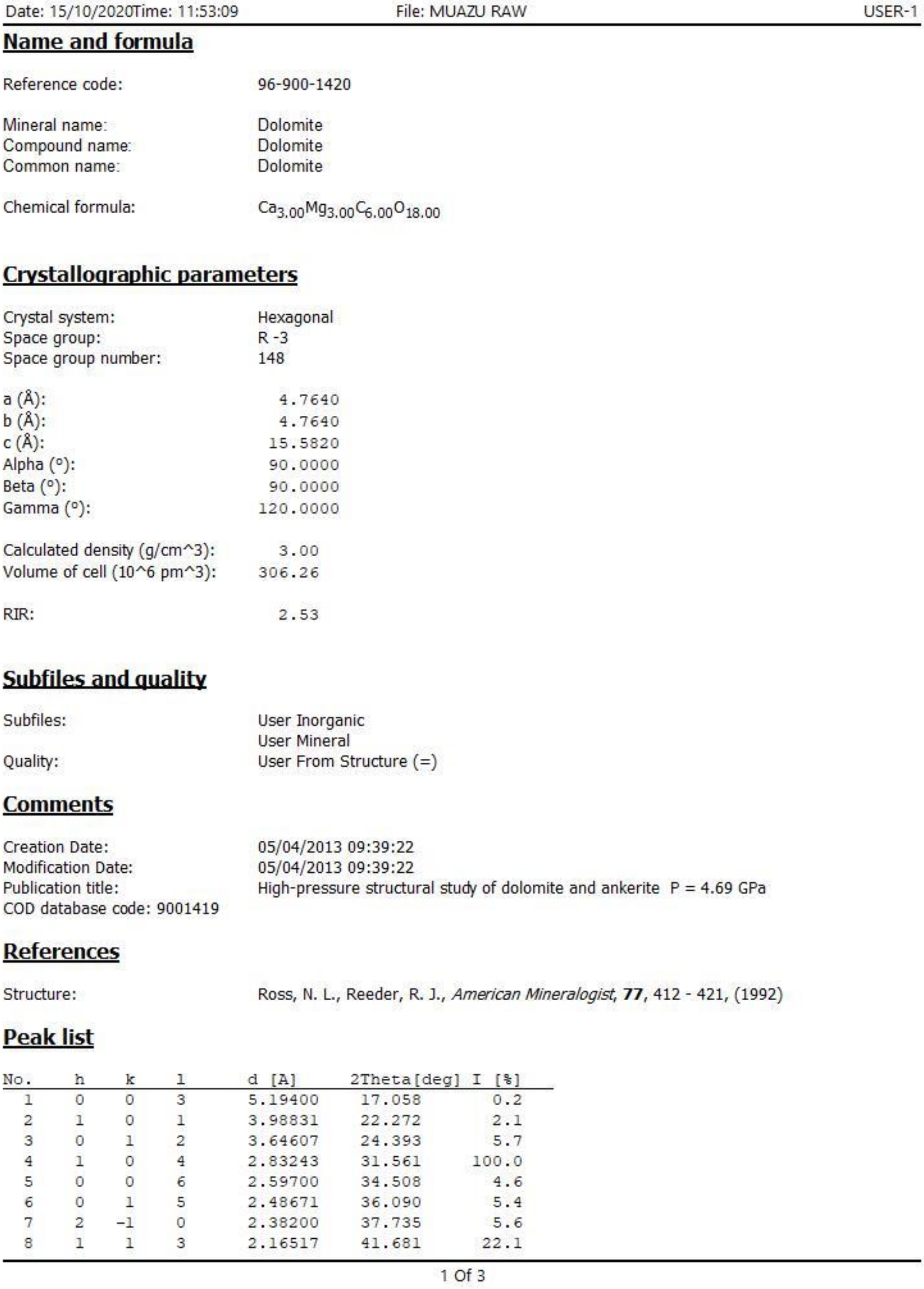
No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	Si	Si	0.53000	0.00000	0.33333	0.4895	1.0000	3a
2	O	O	0.41460	0.14680	0.11876	0.8606	1.0000	6c

Stick Pattern



APPENDIX D

XRD RESULT OF RAW DOLOMITE



Date: 15/10/2020Time: 11:53:09 File: MUAZU RAW USER-1

Name and formula

Reference code: 96-900-1420

Mineral name: Dolomite
Compound name: Dolomite
Common name: Dolomite

Chemical formula: $Ca_{3.00}Mg_{3.00}C_{6.00}O_{18.00}$

Crystallographic parameters

Crystal system: Hexagonal
Space group: R -3
Space group number: 148

a (Å): 4.7640
b (Å): 4.7640
c (Å): 15.5820
Alpha (°): 90.0000
Beta (°): 90.0000
Gamma (°): 120.0000

Calculated density (g/cm^3): 3.00
Volume of cell (10^6 pm^3): 306.26

RIR: 2.53

Subfiles and quality

Subfiles: User Inorganic
User Mineral
Quality: User From Structure (=)

Comments

Creation Date: 05/04/2013 09:39:22
Modification Date: 05/04/2013 09:39:22
Publication title: High-pressure structural study of dolomite and ankerite P = 4.69 GPa
COD database code: 9001419

References

Structure: Ross, N. L., Reeder, R. J., *American Mineralogist*, **77**, 412 - 421, (1992)

Peak list

```
No.    h    k    l      d [A]     2Theta[deg] I [%]
  1    0    0    3    5.19400    17.058       0.2
  2    1    0    1    3.98831    22.272       2.1
  3    0    1    2    3.64607    24.393       5.7
  4    1    0    4    2.83243    31.561     100.0
  5    0    0    6    2.59700    34.508       4.6
  6    0    1    5    2.48671    36.090       5.4
  7    2   -1    0    2.38200    37.735       5.6
  8    1    1    3    2.16517    41.681      22.1
```

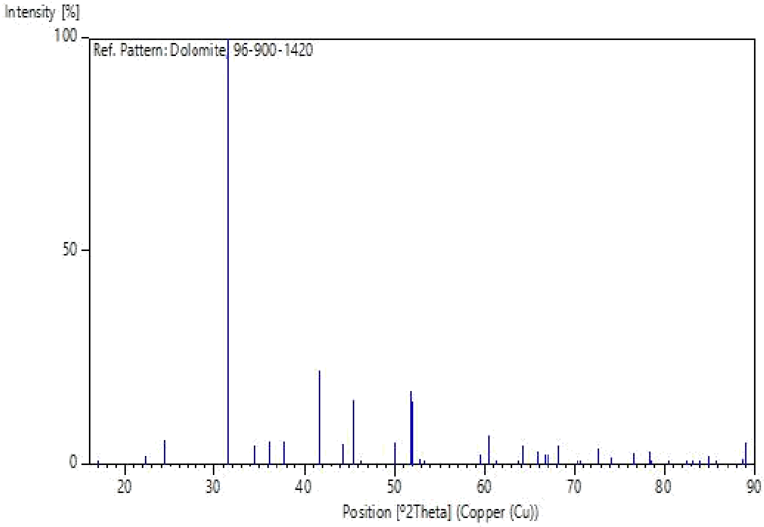
1 Of 3

9	0	2	1	2.04503	44.255	4.7
10	2	0	2	1.99415	45.446	15.0
11	1	0	7	1.95905	46.308	0.4
12	0	2	4	1.82304	49.990	5.1
13	0	1	8	1.76134	51.868	17.1
14	2	-1	6	1.75542	52.056	14.7
15	0	0	9	1.73133	52.836	1.1
16	2	0	5	1.72016	53.206	0.2
17	3	-1	1	1.55163	59.530	2.3
18	3	-2	2	1.52906	60.500	6.9
19	0	2	7	1.51306	61.208	0.1
20	1	0	10	1.45770	63.800	0.8
21	3	-1	4	1.44770	64.293	4.3
22	2	0	8	1.41622	65.901	2.9
23	2	-1	9	1.40048	66.738	2.4
24	3	-2	5	1.39454	67.059	2.3
25	0	3	0	1.37525	68.128	4.4
26	0	1	11	1.33978	70.192	0.0
27	3	0	3	1.32944	70.819	0.2
28	0	0	12	1.29850	72.772	3.6
29	2	1	7	1.27718	74.188	1.8
30	0	2	10	1.24336	76.564	2.8
31	1	2	8	1.21731	78.512	3.0
32	0	3	6	1.21536	78.663	0.2
33	4	-2	0	1.19100	80.597	0.8
34	2	0	11	1.16774	82.547	0.4
35	4	-2	3	1.16087	83.143	0.3
36	1	0	13	1.15102	84.015	0.2
37	1	3	1	1.14120	84.907	0.1
38	1	1	12	1.14010	85.008	1.8
39	3	1	2	1.13213	85.750	1.0
40	3	-1	10	1.10223	88.670	1.1
41	1	3	4	1.09789	89.114	5.0

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	CaA	Ca	0.00000	0.00000	0.00000	0.7604	1.0000	3a
2	MgB	Mg	0.00000	0.00000	0.50000	0.4603	1.0000	3b
3	C	C	0.00000	0.00000	0.24390	0.6498	1.0000	6c
4	O	O	0.03590	0.28550	0.24430	0.8204	1.0000	18f

Stick Pattern


Intensity [%]
100
50
0
Ref. Pattern: Dolomite, 96-900-1420
20
30
40
50
60
70
80
90
Position [°2Theta] (Copper (Cu))