



SUITABILITY ASSESMENT OF AZARA BARITE ORE FOR DRILLING FLUID IN OIL AND GAS INDUSTRY

**MUAZU DANASABE YAKUBU; & HABIBU
UTHMAN**

*Department of Chemical Engineering, Federal
University of Technology, Minna, Nigeria.*

Abstract

In this research, Froth Flotation and purification have been used to assess the suitability of barite ore mined 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 .

Keywords:

Barite, Froth flotation, Drilling mud, Specific gravity and standard comparison.

After the purification operation, the specific gravity value of the beneficiated barite is 4.166 ± 0.029 while the Barium and Sulphur increased to 82.116%

Introduction

Barite, 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. Most crude barite requires some upgrading to minimum purity or density. Barite that is used as an aggregate in a "heavy" cement is

and 9.061% barite with pH of 7 was phases are added with respectively. With purified with 0.2M HCl purification. Therefore froth-flotation, the and a mixture of 0.2M the barite mined from specific gravity values HCl and HOCl. The X- Azara when given obtained were 3.95, ray diffraction patterns required attention its 4.166 and 4.05 show that highly can replace imported corresponding to pH crystalline peaks were drilling mud in Nigeria. values of 5, 7 and 9 obtained after froth respectively. Frothed flotation while more

Crushed and screened to a uniform size. Most barite is ground to a small uniform size before it is used as a 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. 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% of the material, by weight, can pass through a 200-mesh (75-micrometer) (Tyler) screen, and no more than 30%, 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 milligrams per kilogram of soluble alkaline salts (*American Petroleum Institute, 1993*). A small percentage of iron oxide is allowable. 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 milligrams per kilogram of barite (*U.S. Environmental Protection Agency, 1997*). Although barite 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 (Tanko and Shettima, 2015).

The Azara barite deposit is located at about 98 km in Awe local government, south of Lafia the capital of Nasarawa State, Nigeria. The deposit which belongs to the Benue valley system can be described as a Vein and Cavity filling deposit with about 18 Veins. The deposit formed by precipitation from hot barium enriched fields in faults and fractures as a result of fluid mixing at reduced pressure and / or temperature. Sometimes the fluid dissolves the surrounding host rocks to form irregular replacement deposits (Smith, 1978). Some of the vein deposits dip at an angle of 70°, while others are at an angle of 45°. The over burden on the veins vary from about 10m to about only 1.5m – 2m. The depth of some of the vein outcrops vary from about +8m above ground level to about -10m below ground level (Nzeh and Hassan, 2017).

Barium sulphate ($BaSO_4$) often occurs as large veins or beds, as gangue mineral in various mineral veins, in limestone's, sandstones and like deposits. The ores are generally low grade and require concentration by floatation to meet market specifications. 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 (Nzeh and Hassan, 2017).

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. 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 (Nzeh and Hassan, 2017). 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. Barite is generally easy to identify. 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 just three observations (Nzeh and Hassan, 2017).

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, i.e., 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 sulfide 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 13500:2008(E)).

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. Other minerals such as siderite, dolomite and pyrrhotite are not covered in this International Standard, but can cause undesirable performance in some drilling fluids. 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. 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 13500:2008(E)).

Drilling-grade barite is 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. For the gravity separation of barite, the processes involved are: crushing, screening and jigging. Then the high grade (over 80%) concentrate resulted. Jig is the main equipment for the separation and purification of barite ore. It saves energy; possess high efficiency and environment protection. In the process of crushing, jaw crusher was employed and two-stage crushing processes were applied. In the process of screening, simple and useful circular vibrating screen was employed, 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 separate the coarse and fine granularity of barite material respectively (Jameson, 1992).

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. It 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" (Jameson, 1992). 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 (Jameson, 1992).

Materials and Method

Sample Preparation

The barite ore samples as received were broken manually with sledge hammer to provide a required size acceptable to laboratory was first crushed using a Jaw crusher until the particle sizes were less than 1180 μm .

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.

In Coning and quartering:

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 & 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 10 mins with sieves of sizes +180 μm , +90 μm 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.

Sample Characterisation

The specific gravity of the barite ore was determined before and after the beneficiation process. This was done by washing the sample thoroughly, weighing an empty pycnometer bottle and recording the weight. The 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:

Specific Gravity

$$SG = \left\{ \frac{\text{Weight of Mineral in Air}}{\text{Weight of Mineral in Air} - \text{Weight of Mineral in Water}} \right\}$$

The chemical analysis of the barite ore was determined using X-ray Fluorescence. 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 leaching processes. The phases present in the sample were determined using X-ray diffraction (Bruker D8 diffractometer) equipped with CoK α 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.

Results and Discussion

Chemical Composition Analysis

Table 1 shows the results of the chemical composition analysis for barite sample before and after the beneficiation process. 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 11.14%. When the amounts of Ba and S are added together, they make up about 68.6% while Fe also has a very significant quantity contributing about 10.1%. This is similar to the composition in the literature concerning Azara barite. The amounts of Ba in the barite after froth floatation and purification with HCl increased to 82.2 and 92% respectively. The amounts of the other elements decreased to 5.2% and <1% after froth flotation and purification with 0.2M HCl respectively.

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

OXIDE	HEAD SAMPLE	CONC.	TAILING
<i>LOI</i>	3.112	3.000	5.040
<i>SiO₂</i>	15.411	5.350	64.020

<i>CaO</i>	0.443	0.085	1.121
<i>SO₃</i>	20.042	9.061	15.247
<i>Fe₂O₃</i>	0.300	0.202	0.216
<i>CuO</i>	0.067	0.027	0.075
<i>ZnO</i>	0.043	0.003	0.008
<i>Rb₂O</i>	0.002	< LOD	< LOD
<i>SrO</i>	0.438	0.110	0.863
<i>ZrO₂</i>	0.008	< LOD	0.002
<i>Eu₂O₃</i>	0.081	< LOD	< LOD
<i>BaO</i>	56.224	82.116	13.403
<i>Re₂O₇</i>	0.002	< LOD	0.004
<i>PbO</i>	< LOD	< LOD	< LOD
Total	99.999	99.999	99.999

LOD: Low Detection

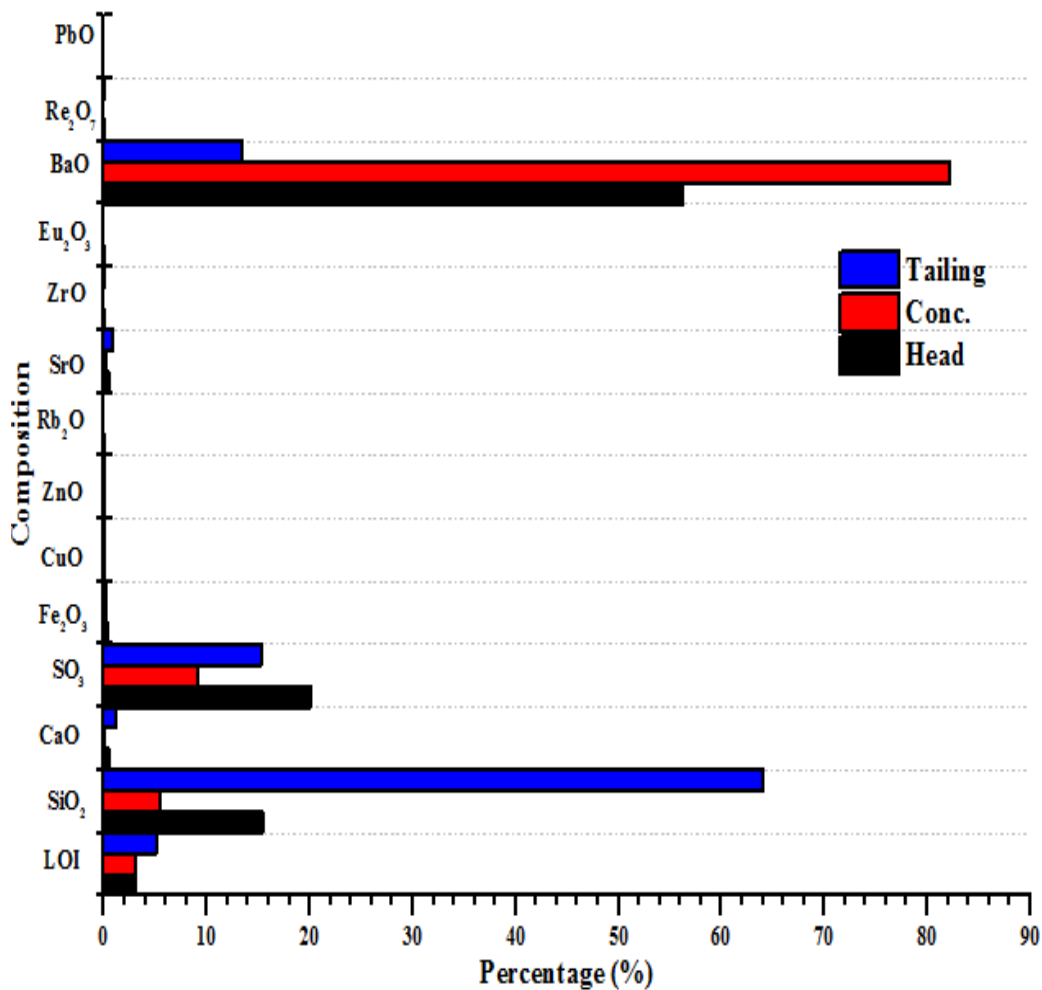


Fig. 1: Percentage Concentration of various Component of Barite Ore

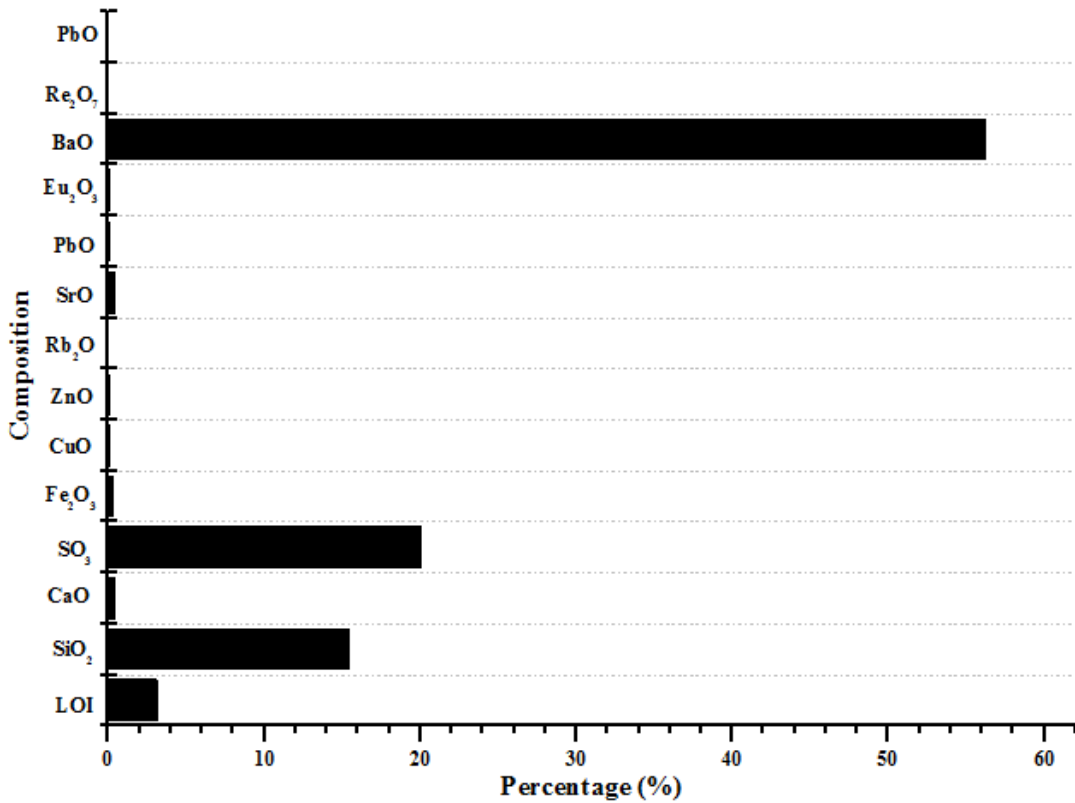


Fig. 2: Concentration of component before flotation of Barite Ore

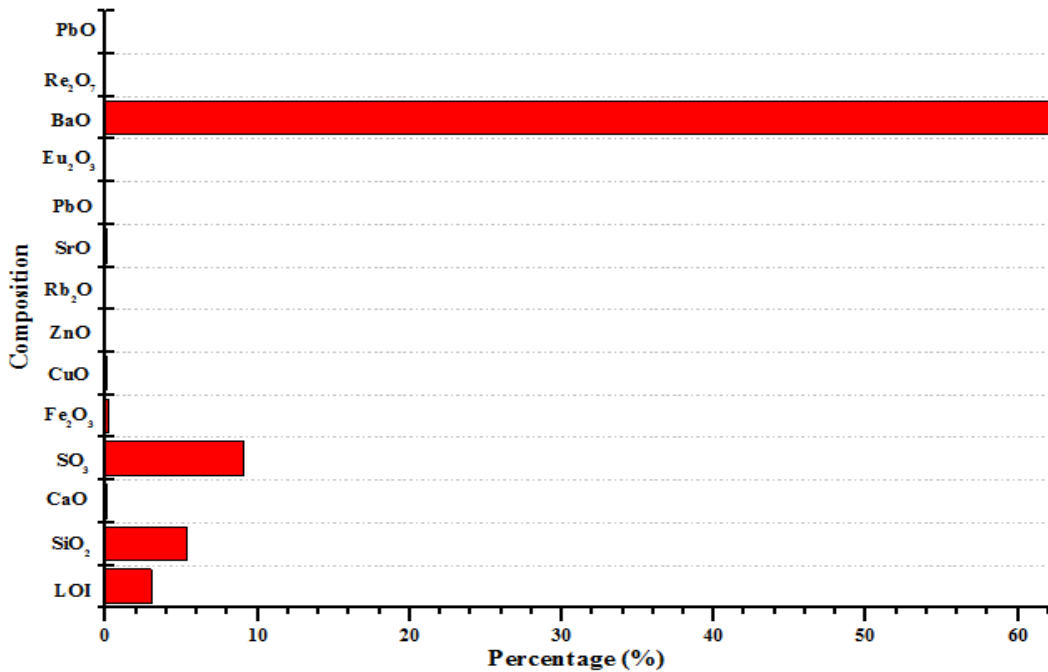


Fig. 3: Concentration of component after flotation of Barite Ore

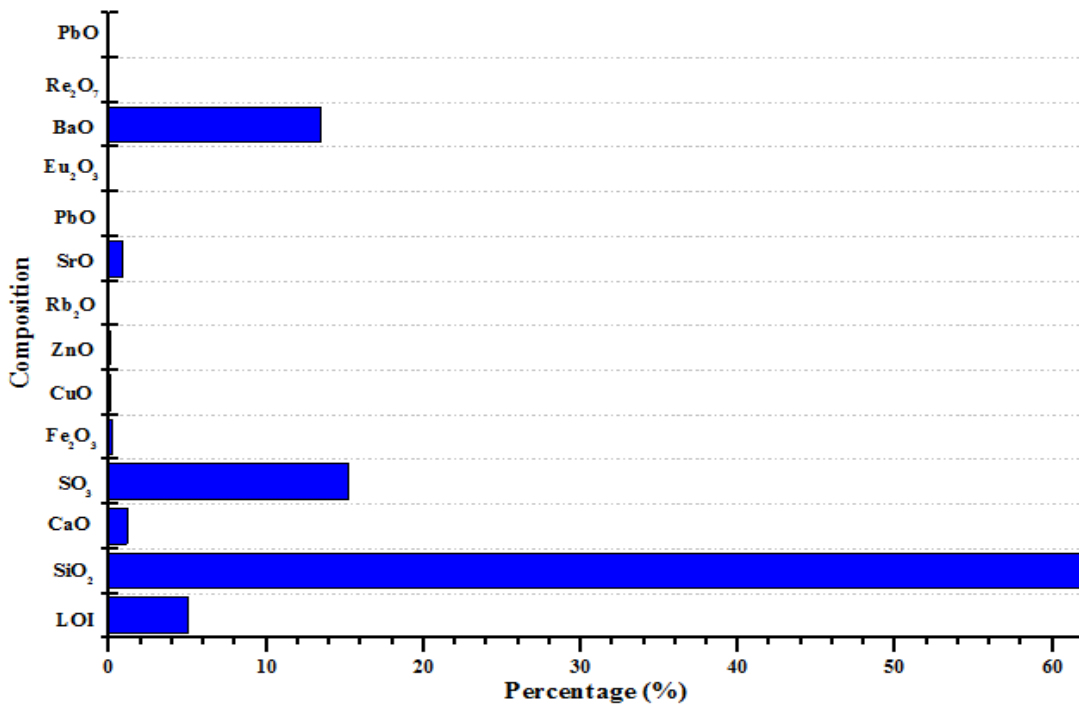


Fig. 4: Concentration component of tailing/gangue

FROTH FLOTATION

Two hundred grams of the sample obtained from the sieve of 125 μm subjected to flotation experiments where 30% w/w solid to liquid pulp were prepared. This pulp poured into laboratory Denver flotation cell and well mixed with impeller speed of 1500rpm. After that, depressant (Sodium silicate), collector (Oleic acid) were added to the pulp, and conditioning (without air) was done for about 10 minutes, 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.

Table 2: Result of purification of the Barite Ore

Particle Size	Products (Barite)		
	Feed	Concentrate	Tailing
-125 μm +90 μm	200g	26.19g	162.98
	100%	13.095%	81.49%

Purification and froth flotation

The result of the froth flotation process that was carried out on the Azara barite is shown in Table. 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%, 67.24% and 70.74% respectively. The amounts of the depressed minerals are 32.37%, 31.55% and 28.33% 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 9.061 % while that of barium increases to 82.116%. The concentration of barium in the froth at different pH values indicate that 81.8% was obtained at a pH of 5, 82.116% at pH of 7 and 79.86 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 3.957 ± 0.017 , 4.166 ± 0.026 and 4.054 ± 0.01 respectively.

X-ray Diffraction

Figure below shows the X-ray diffraction patterns for Azara barite ore, a fitting of the barite ore with reference pattern (barite) in the ICDD database shows that it contains about 75% of 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. 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 froth flotation was also analysed with the reference from the database for barite (96-900-4123) and found to contain about 86% barite.

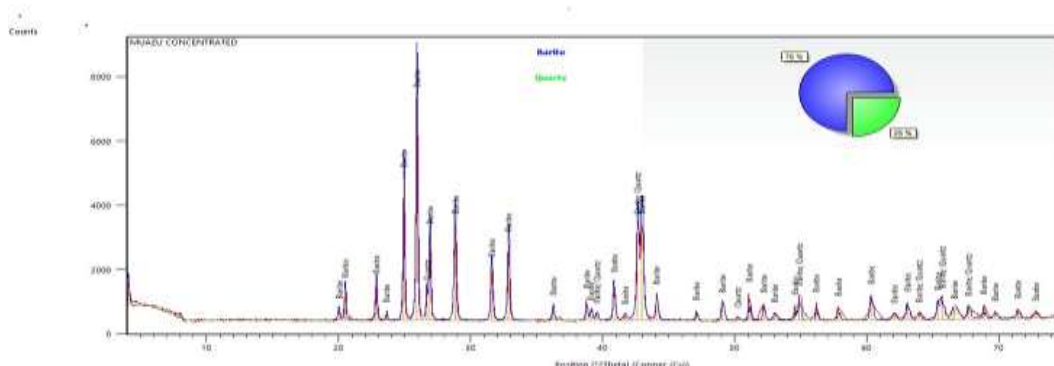


Fig. 5: X-ray Diffraction of Barite Ore

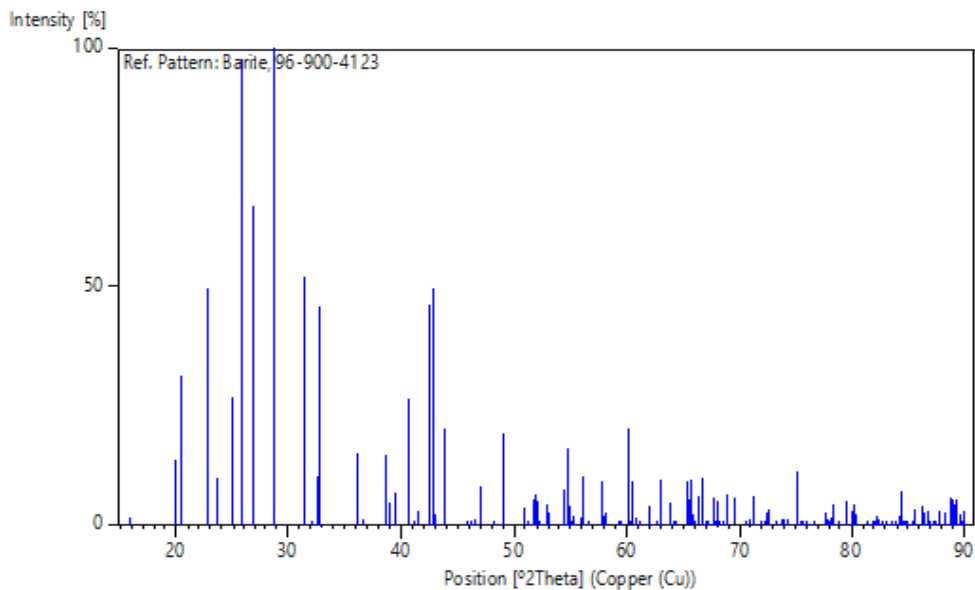


Fig. 6: X-ray Diffraction of Raw Barite Ore

Conclusions

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. Its therefore be concluded that purification improved significantly the beneficiation of Azara barite ores.

REFERENCE:

Achusim-Udenko, A. C. Gerald, O. Martins, O. and Ausaji, A. "Flotation Recovery of Barite from Ore Using Palm Bunch Based Collector" *Int. J. Chem. Sci.*, vol. 9, pp. 1518-1524, 2011. Chen, Z. Ren, Z. Gao, H. Qian, Y. and Zheng, R. "Effect of modified starch on

- separation of fluorite from barite using sodium oleate," *Physicochemical Problems of Mineral Processing*, 2017.
- Tanko, I. Y. Adam, M. and Shettima, B. "Petrology and Geochemistry of Barite Mineralisation around Azara, North Central Nigeria," *International Journal of Scientific and Technological Research*, vol. 4, pp. 44-49, 2015.
- Grigorova, I. Dzhamyarov, S. and Nishkov, I. "Barite Flotation Concentrate From Kremikovtzi "BL ACK" T lings," *Journal of International Scientific Publications-Materials, Methods & Technologies*, vol. 9, pp. 561-577, 2015.
- Nzeh, N. S. and Hassan, S. B. "Gravity Separation and Leaching Beneficiation study of Azara Nassarawa Barite Mineral Ore," *Global Journal of Researches in Engineering: J General Engineering*, vol. 17, 2017.
- Raw Materials Research and Development Council, "Non-Metallic Mineral Endowments in Nigeria," Abuja: Federal Ministry of Science and Technology, pp. 1-113, 2016.
- Strbac, N. Sokic, M. Zivkovic, D. Matkovic, V. and Markovic, B. "Environmentally Friendly Complex Sulphide-Barite Ore Treatment by Leaching in Ferric Chloride Solution," in *4th International Symposium on Environmental and Material Flow Management - EMFM14*, Bor's lake, Serbia, 2014.
- Wang, H. J. Dai, H. X. Yang, W. L. and Li, T. T. "Research on the Flotation Experiment of a Low-Grade Barite Ore in Myanmar," *Applied Mechanics and Materials*, vol. 644-650, pp. 5277-5280, 2014.
- ISO 13500:2008(E) International Standard for Petroleum and natural gas industries — Drilling fluid materials — Specifications and tests 3rd Edition 2008.