Assessment of some baryte ores from Northern Cross-River, Nigeria, for oilfield drilling fluid supplement

Debrah Memshima Oahimire¹, Victor Uchechi Ukaegbu², Joel Friday Ogbonna¹

¹ World Bank Africa Centre of Excellence, Centre for Oilfield Chemicals Research, University of Port Harcourt.
² Department of Geology, University of Port Harcourt, Rivers State, Nigeria

*corresponding author: debrah.oahimire@gmail.com

Abstract

There is a very high demand for the American Petroleum Institute (API) grade baryte in Nigeria due to the continuous massive drilling in oil and gas fields. Considering the presumption that local baryte is of low quality, processed baryte is imported, leading to immense national revenue losses. Some baryte deposits in the Northern Cross River, Nigeria, were sampled and studied in field and laboratories, based on API standard requirements (2004 and 2010), to ascertain their suitability for use as weighting additive in drilling fluids. Furthermore, flame testing of the samples yielded yellowish-green flame indicating barium presence; X-ray diffraction (XRD) and X-Ray fluorescence (XRF) analyses confirmed the mineralogy and chemical composition of the samples, respectively. The results revealed the Specific Gravity, SG range of 4.37 to 4.52; concentration of alkali earth metals as calcium 8.40mg/kg to 62.10 mg/kg to 62.10 mg/kg; the residue >75 micron and particle sizes <6microns processed had normal range, respectively below 3% and 30%; and the samples’ BaSO₄ %weight composition was over 90%. The chemical analysis indicated no significant undesired minerals. Galena gangue with baryte was observed in three locations though these could be easily beneficiated through physical separation. The tests and analyses result qualified the Northern Cross River baryte samples as high-grade API standard baryte, suitable for oilfield drilling fluid. Further estimation of the baryte reserves in this region was highly recommended, as this might proffer a substantial solution to the sustainable supply of excellent local quality drilling baryte in Nigerian oilfields.

Keywords:
API standard requirement, baryte, Benue Trough, oil fields drilling fluid, quality evaluation

Introduction

Baryte is an industrial mineral, a well-desired weighting material in oilfield drilling. Among several materials, it is a supplement in drilling fluids that serves different functions. As a weighting material, baryte is primarily used to increase the density of drilling mud up to 21 lb/gal (2.5g/cm³) (Ariffin, 2004) to exercise control against over-pressured formations and prevent kicks and blowouts through borehole stabilisation, and for well control applications from solid-laden plugs. Almost all drilling fluids contain baryte, which could be approximately 10% and 40% (by weight) in low-weighted oil-based muds and highly weighted oil-based muds, respectively (Bosch, 2016). Even though worldwide, the relative consumption of baryte seems to have a declining trend, baryte still finds relevance in certain areas of oil and gas drilling activities. There are substitutes to baryte (but not without challenges), used as weighting agents, such as galena, PbS, calcite (CaCO₃), dolomite, (CaCO₃ MgCO₃), iron ores like ilmenite (FeO.TiO₂),...
siderite \((\text{FeCO}_3)\), and haematite \(\text{Fe}_2\text{O}_3\), including recent synthetic haematite produced in Germany (not yet extensively used, tested and proven like baryte) \((\text{Ariffin}, 2004)\). These substitutes have not been proven to have high-performance competitiveness like baryte in price and quality, and so, they have no major market impact on drilling muds composed of baryte \((\text{McRae}, 2020)\).

Baryte is preferred as the appropriate weighting additive for drilling fluids in oil and gas fields because of its unique qualities, which, according to Darley and Gray \((\text{1988})\), include its high specific gravity of up to 4.5, physical and chemical inertness, low solubility, relative softness \((3-3.5\) hardness\) and low abrasive quality, relatively low or moderate cost, bulk availability, non-toxicity and environmental friendliness, low oil absorption, and additionally, low interference with magnetic measurements retrieved in boreholes, or in logging-while-drilling or in isolated drill-hole logging \((\text{McRae}, 2016)\). The SG of baryte is considered to be its most essential characteristic for use in drilling mud \((\text{McRae}, 2016)\).

This study is predicated on the wide gap that exists between the demand and supply of local drilling grade, also known as the API grade baryte. This is following the general assertions from some stakeholders that, basically, Nigerian baryte does not meet the API standard requirement \((\text{O’Driscoll}, 2017; \text{Energy Mix}, 2019; \text{Kadiri}, 2020)\), among others, and the standard quality is not enormous to cater for the country’s industrial need. This presumption has economic implications as it is at Nigeria’s expense—losing large funds for importation. There is massive capital flight as much as \text{N}5bn per annum, job exportation, and generally, some developmental setbacks against the solid mineral and the people \((\text{Ovadia 2013; O’Driscoll, 2017; Al-Awad et al., 2019})\). However, considering the API set standard \((\text{McRae, 2016})\), this included about 90% weight \(\text{BaSO}_4\) gravity, SG of 4.2 minimum specified in API standards \((\text{McRae, 2016})\), as seen in Tables 1.a and b.

As relevant and essential as baryte is in the Nigerian oil industry, the commodity is underdeveloped and mined mainly by artisanal and low scale miners, effectively resulting in very high demand \((\text{Foraminifera Market Research Limited, 2016})\). According to the Nigeria Geological Survey, NGS (Figure 1) and Ministry of Mines and Steel Development, MMSD, \((\text{2008})\), the country has over 21 million tons of baryte inferred resources concentrated in the Benue Trough. Meanwhile, the initiative of the government to ban baryte importation again to develop the local baryte resources is still in the pipeline \((\text{Energy Mix Report, 2019; Kadiri, 2020})\). This decision calls for proactive research on the subject of baryte to ascertain and establish the quality and quantity. Some major oil companies like Chevron Nigeria Ltd., Total E and P, and others have at various times made collaborative moves with academia, mining and processing companies to encourage research and development, aimed at increasing production and supply of good quality local baryte, enhancing its development, import reduction and indigenous job creation \((\text{Ovadia, 2013; Chevron Nigeria Ltd., 2017; Adefedeji et al., 2018; Energy Mix, 2019})\). Hence, this research evaluated the quality of the Northern Cross River baryte to ascertain the adequacy for use as a weighting material in drilling mud, based on API \((2004\) and \(2010)\) required standards. It suffices to say that the study is further motivated by the foregoing expressed challenges, a massive gap between local baryte supply and demand, which continues to orchestrate the expeditious importation of baryte API grade baryte and the resultant massive losses.

Previous studies in this area date back to 1951 \((\text{Bogue, 1951})\), with reported prospects of baryte in the Gabu part of Northern Cross River. In 1952, there was a report of baryte galena and sphalerite veins occurrence as gangue \((\text{Farrington, 1952})\); and there are some later regional studies involving quality of barytes in the Benue Trough, economic potentials of Baryte in Southern Benue Trough, reviews of past research and, determination of some baryte suitability in drilling fluid simulations; all these expressed recommendations for further work \((\text{Ene et al., 2012; Oden, 2012; Lobe et al., 2018; Duru et al., 2019})\), among others. Although as of 2016, it was reported that there were about 2 million metric tons of baryte scattered all over Plateau, Nasarawa, Benue and Cross River states. More recent reports place the estimation of Cross River baryte reserves alone at over 9 million and 11 million tons \((\text{Energy Mix Report, 2019; Obi et al., 2019})\). This is encouraging for industrial exploitation of the resource. The API set standard requirements for the quality of baryte to be used as a weighting material in drilling mud; the most important of these, according to \text{McRae (2016)}, is the specific gravity, SG of 4.2 minimum specified in API Specification 13A \((\text{2004})\). However, considering declining reserves of 4.2-SG baryte, the API released an updated version of API Specification 13A, Specification for Drilling Fluids Materials, accommodating a minimum 4.10 SG baryte with all other specifications same as in the previous 4.2 SG baryte, with effect from August 1, 2010 \((\text{API, 2010; McRae, 2016})\); this included about 90% weight \(\text{BaSO}_4\) in both API specifications \((2004\) and \(2010)\); \text{Al-Awad and Al-Qasabi, 2000; Mineral Galleries, 2001; Johnson et al., 2017) as seen in Tables 1.a and b.
Study Area Location and Accessibility

The studied area is a transitional area located between the Lower and the Middle Benue Trough, Figures 1 and 2. It has a northern boundary with Benue State and extends southwards towards the Lower Benue Trough. There is a general logistics challenge: the minefields are located in underdeveloped countries, and the link roads to the mines are essentially so deplorable that they are scarcely plied by motorists. There are also insecurity concerns, lack of data and other challenges.

Figure 1. Simplified geological map of Nigeria showing baryte deposits locations and the study area. Source: (Modified after NGSA, 2011, map retrieved from Kadiri, 2020).

Regional geological setting; physical, chemical and technical highlights

The regional geology of Nigeria is made up of hard rocks (igneous and metamorphic rocks) and soft rocks (sedimentary rocks) Figure 1. Baryte, generally, could be formed and found in any type of these rocks. However, the baryte ores deposits in Nigeria are predominantly located in the sedimentary basins especially in the Benue Trough. This is an extensive structural basin over 800km long and about 180-250km wide, striking NE-SW and infilled with over 5,000m thick Cretaceous sediments, overlying the Pan African Basement rocks (Benkhelil 1982; Guiraud 1993). The Benue Trough has several primary and secondary mineralisations.

Baryte generally occurs in three ways according to King (2013) viz: (i) Vein and cavity filling, e.g. Hydrothermal veins: baryte is formed as barium rich epithermal fluids flow into faults, joints, cracks, voids, cavities, bedding planes and any other points of weakness or openings and crystallises in the host rocks; (ii) Residual deposits; as the name implies these are secondary deposits formed as residues of the weathered sediments and sedimentary rocks having concretions of primary baryte mineralisation; and (iii) Precipitate (bedded) Stratotype form for instance, where baryte precipitate from seawater – rather than traction – forming beds of deposits with lateral extents (Ariffin, 2004). From field observation of this work, the baryte in the study area were predominantly formed as swarms of hydrothermal veins approximately 1m to <5m wide and some hundreds of meters in length, except as observed in the Alifokpa mine, where the setting of the baryte deposits is more like bedded type, overlain by thick top weathered overburden (Figure 3), as also noted in Oden (2012). Pitting and trenching are the common techniques in the mines. Host rocks include clays, shales, sandstones and conglomerates. Baryte naturally occurs as BaSO$_4$ and generally has several mineral associations. It often forms a solid solution with celestite SrSO$_4$, forming BaSrSO$_4$, and may occur with some other Sulphate minerals like anhydrite CaSO$_4$, anglesite (PbSO$_4$), isomorphs which constitute the baryte group (Hanor, 2000). The mineral is mostly discovered with ores of antimony, cobalt, copper, lead, manganese and silver (King, 2013). It may also occur with witherite BaCO$_3$, galena PbS, sphalerite (Zn, Fe)S, quartz, chalcopyrite, pyrite, aragonite, fluorite, cerussite, among others (Mineral Galleries, 2001). Lead-Zinc-Baryte is an established mineral association identified in the Benue Trough Figure 2 (Ene et al., 2012; Ogundipe, 2017; Labe et al., 2018).
Figure 2. Distribution of lead-zinc-baryte mineralisation along the Benue Trough (Inset sketch map of Nigeria showing the Benue Trough) [modified from Ene et al. (2012)- after Cratchley and Jones (1965) and Labe et al. (2018).

The drilling baryte is expected to be about 90 weight % of BaSO$_4$ (Al-Awad and Al-Qasabi, 2000; Johnson et al., 2017). Generally, baryte may be colourless and transparent, but it also has a variety of colours: white, yellow, green, grey, brown and so on, because of various elemental and mineral impurities like strontium, iron, lead, etc.; and sand, clay, etc. respectively (Foraminifera Market Report, 2016). It has a vitreous lustre, unidirectional cleavage and maybe tabular. It has a molecular weight of 233.43, contains 65.7% of BaO, 34.3% of SO$_3$, and is occasionally found with Strontium and Calcium as isomorphic admixture (Betekhin et al., 1964). Baryte has a specific gravity, SG of up to 4.50, hardness 3-3.5. Practically, baryte of any colour could be used in drilling muds (McRae, 2016). For this work, the samples taken from the field of study had different colours, like pure white, pearly white, yellow, light grey, and transparent glassy varieties. Baryte’s desirable physical and chemical properties make it have various uses in several industries like glass making, paper and paint, medical and pharmaceutical, chemical, plastic, metallurgical, automobile, concrete, ceramic, oil and gas, etc. (Pulidindi and Pande, 2017). Baryte is used in the oil and gas industry than any other for the formulation of drilling mud. The functions of drilling mud are highlighted in Shearn (2010).

**Undesired materials in drilling muds**

The unwanted materials include some environmentally common, naturally occurring accessory minerals that might be abrasive (like silicates, e.g. quartz and chert) and are likely to cause excessive wear and tear to the drilling bits, reducing the bit’s life span; minerals that are soluble like Gypsum (calcium sulfate dihydrate,
CaSO₄·2H₂O) and in the presence of hydroxyl ions are capable of releasing potential harmful cations like calcium, an alkaline earth metal which has a standard concentration threshold of 250 mg/kg in a grounded baryte (Table 1a) prescribed by API (API 2004 and 2010; McRae, 2016); and minerals that are insoluble like dolomites (calcium magnesium carbonate (CaMg(CO₃)₂), and Pyrrhotite (Fe₁₋ₓS) but in the presence of hydroxyl ions are capable of releasing potential acidic and harmful anions like carbonates and sulphides respectively, (Shearn, 2010). Standards regulating the concentrations of these impurities have not been developed owing to their insoluble nature (McRae, 2016). The presence of impurities is capable of reducing the density of the baryte and affecting the distribution of particle sizes of the grounded baryte. For this reason, API (2004 and 2010) stipulates that the baryte for mud use be finely grounded and that on sieving, 97% of it by weight should go through a 75 microns (µm) mesh (that is, the material should not contain more than 3% of particle sizes that are above 75 µm) and not more than 30% of the grounded material, by weight, should be less than 6 µm in equivalent spherical diameter, where this diameter is determined by sedimentation method (API, 2004 and 2010; McRae, 2016).

**Materials and Methods**

**Geological fieldwork** was done in the Northern part of Cross River, Nigeria and samples were taken from baryte mines located at Alifokpa, Osina, Gabu in Yalla and Okumurukhet in Obubra, Figure 4. The field samples were identified in hand specimen using cleavage, relative heaviness by heft tests, etc. as barytes with various colours like pure white, pearly white, glassy (transparent) white, brown, grey and yellow (Figures 3, 5, 6, 7 and 8), some with inclusion (Figure 2d). Multiple colours of baryte are practically used in petroleum drilling (McRae, 2016). However, systematic identification and confirmation of the identity of the samples were necessary to be done beyond a reasonable doubt, especially considering that the presence of impurities, which causes the colour variation, could raise or lower the specific gravity of lower grade baryte and influence or mislead interpretation of the identity. Heft testing was done on the spot, comparing the heaviness of the samples relative to other materials; and other diagnostic features like cleavage were observed, then the mineral baryte was identified in the first instance based on its relative weight and its characteristic three right-angled cleavages, subject to further investigation.

Figure 4. Map of study area showing sampled locations and some mines status in Northern Cross River.

Figure 5 Osina barytes: (a) broken transparent, tabular, glassy white, (b) pearly white with clay stains. (c) the yellow, glassy broken tabular baryte with some inclusions; XRD revealed the only baryte.
Laboratory tests

Flame test
A flame test was carried out to ascertain the presence of barium-sulphate and distinguish it from other possible heavy mineral associations (plates 8a), being mindful of associated sulphates, especially that celestite, SrSO$_4$ forms a solid solution, BaSrO$_4$ (Bonel, 2005). The flame test is simply done by subjecting a few grams of the sample chip or powder to a gas flame. The presence of BaSO$_4$ turns the blue gas flame to yellowish-green with varying intensity depending on the barium sulphate content. Conversely, Sr in celestite (SrO) yielded a reddish flame.

The API 2004 and 2010 specification tests 13A for the samples (Table 1)
The specific gravity (SG) being the most crucial property was done in two different laboratories independently using the Le Chatelier Flask prescribed by API manual 13A. All samples were properly washed and dried, pulverised and sieved through a 75 µm mesh, and then 80g was taken for the SG test, 100 g for the water-soluble alkaline earth metals as Ca, 50g for the residue of diameter >75 µm and 80g for particles <6 µm in equivalent spherical diameter, determined by sedimentation method. The above tests procedures followed the API 2004 standard guide (manual). The pH values were obtained by dipping pH strips in the baryte suspension in distilled water.

Mineralogy
The mineralogy of samples was established and confirmed through the X-Ray powder diffraction technique using a Panalytical Empyrean XRD diffractometer of NGS. It is a non-destructive analysis. A few grams of the washed and dried samples were pulverised using steel and agate mortars, the samples were compacted and flattened on a sample holders rack, and the bulk mounted on the sample stage in the goniometer - the central working system of the diffraction unit. In this XRD technique, X-rays are generated and made to pass through the targeted samples, and the intensity, I, of the diffracted rays are processed and converted to count rate, which is sent to a computer device (a monitor and printer). The operation is based on Bragg’s law. Many inorganic compounds like minerals have database files for d-spacing as Powder Diffraction Files (PDF), provided by The International Centre for Diffraction Data. With the aid of Xpert Highscore Plus software from Panalytical, automated search matching of the d-spacing/diffractogram peaks of the samples (considered unknown) was done against the d-spacing/diffractogram peaks of standard known minerals. By doing so, the identity of minerals composed in the sample was conclusively diagnosed.

| Requirement                          | API Specification |
|--------------------------------------|-------------------|
| Specific Gravity (API 2004)          | 4.2 minimum       |
| Specific Gravity (API 2010)          | 4.1 minimum       |
| Water-soluble Alkaline Earth Metals as Ca, | 250 mg/kg maximum |
| Residue > 75microns (µm)             | maximum mass fraction 3.0% |
| Particles < 6 microns (µm)           | maximum mass fraction 30% |
| In equivalent spherical diameter      | Source API 13A (2004) 16th Edition and API 13A (2010), 18th Edition. |

Table 1b. Some other additional requirements.

| Requirement       | API Specification |
|-------------------|-------------------|
| Moisture content  | 1%                |
| Oil Absorption    | 9%                |
| pH                | 7                 |
| BaSO$_4$          | 90% Minimum       |

Sources: Al-Awad and Al-Qasabi 2000; Mineral Galleries, 2001; Johnson et al., 2017)

Geochemical analysis
The geochemical method used in the study was the Energy Dispersive X-Ray Fluorescence (EDXRF) through the Minipal 4 EDXR machine. The method for
determining Loss on Ignition (LOI) was gravimetry – using a furnace. A few grams of each sample were pulverised in a motorised agate mortar and sieved to <53µm; then about 10g of it was mixed with 1g stearic acid to bind and was well homogenised in an agate mortar. The mixture was then pelletised by placing the sample on a 40mm diameter hardened steel disc and pressing it with a 25-ton hydraulic pressure press. The produced pellets were then analysed for major oxides, which in turn aided weight %BaSO₄ calculation.

Results and Discussions

Fieldwork results

The baryte identified from hand specimen study, including hefting, had various colours like pure white, pearly white, yellow (amber), grey. There were transparent, translucent and very impressive tabular varieties (Figures 3b, c, 5, 6, 7 and 8). The mineral association identified with the baryte includes quartz, galena, antimony, salt springs, garnets, etc. Quartz is generally common with variety, including amethyst, especially in Obubra; galena, PbS was prominently observed as a gangue mineral in Alifokpa-Gabu in Yalla (Figure 3b) and Okumurukhett in Obubra baryte deposits (Figure 8.). The Gabu barytes are also associated with salt springs and antimony. The host rocks for the baryte in the study area include sandstones, shales, siltstones, clays, and conglomerates.

Laboratory results

Flame test results

All the samples tested positive, suggesting the presence of barium-sulphate in the samples. Progressively, their actual percentage composition was determined and confirmed by subsequent chemical analysis. Furthermore, various analyses were carried out, as indicated below in this write-up.

API Requirement Tests: (API 2004 and 2010 Specification 13A)

Table 2. Results of the API 2004 and 2010 specified physical and chemical tests for barytes.

| Requirement               | API Specification     | Results                          |
|---------------------------|------------------------|----------------------------------|
|                           | Alifokpa Yala          | Osina Yellow Yala                | Osin 3 White Yala | Gabu 1 Yala | Gabu 2 Yala | Okumurukhett Obubra |
| Density Lab1              | 4.20 g/cm³, min.       | 4.42                            | 4.47              | 4.52       | 4.40       | 4.51               | 4.44               |
| Density Lab2              | 4.20 g/cm³, min.       | 4.37                            | 4.44              | 4.42       | 4.44       | 4.42               | 4.40               |
| Alkaline Earth Metals as Ca | 250 mg/kg maximum     | 8.40                            | 16.96             | 62.10      | 40.18      | 44.8               | 40.40              |
| Particles >75 µm          | 3.0 Weight %, maximum | 0.44                            | 0.34              | 0.54       | 0.6        | 0.50               | 0.66               |
| Particles <6 µm           | 30 Weight %, maximum   | 20.80                           | 17.62             | 22.10      | 20.12      | 26.4               | 24.00              |
| Moisture Content in %     | 1%                     | 1.4                             | 1.0               | 1.8        | 1.0        | 0.8                | 1.5                |
| pH                        | 7 (Neutral)            | 7                               | 7                 | 7          | 7          | 7                  | 7                  |
XRD Results

Table 3. XRD results (peak values at 100% intensity, I).

| No | Sample               | Minerals  | Spacing d, (Å) | 2Theta[deg] | Diffractogram Reference |
|----|----------------------|-----------|---------------|-------------|-------------------------|
| 1  | Alifokpa             | Baryte    | 3.10391       | 28.739      | Figure 9                |
| 2  | Osina Yellow         | Baryte    | 3.10244       | 28.753      | Figure 10               |
| 3  | Osina3 White         | Baryte    | 3.10244       | 28.753      | Figure like 10          |
| 4  | Gabu 1               | Baryte    | 3.10244       | 28.753      | Figure 11               |
| 5  | Gabu 2               | Baryte    | 3.10244       | 28.753      | Figure like 11          |
| 6  | Okumurukhtet Obubra  | i. Baryte | 3.10391       | 28.739      | Figure 12               |
|    |                      | ii. Galena| 2.96800       | 30.085      |                         |

Some of the XRD general diffractograms for the Northern Cross River baryte samples:

Figure 9. XRD – general diffractogram for Alifokpa: baryte

Figure 10. XRD – general diffractogram for Osina Yellow: baryte.
Figure 11. XRD – general diffractogram for Gabu1: baryte.

Figure 12. XRD – general diffractogram for Okumurukhtet Obubra: baryte and galena.

**XRF results**

Table 4. XRF results for Northern Cross River baryte samples.

| Oxides | Alifokpa Yala | Osina Yellow Yala | Osina 3 White Yala | Gabu 1 Yala | Gabu 2 Yala | Okumurukhtet Obubra |
|--------|---------------|--------------------|--------------------|------------|------------|---------------------|
| SiO₂   | 0.30          | 0.26               | 0.28               | 0.30       | 0.32       | 0.29                |
| TiO₂   | <0.001        | <0.001             | <0.001             | <0.001     | Nd         | 0.114               |
| Al₂O₃  | <0.001        | <0.001             | <0.001             | <0.001     | <0.001     | 1.29                |
| Fe₂O₃  | 0.01          | 0.020              | 0.019              | 0.013      | 0.01       | 0.077               |
| CaO    | 0.15          | 0.09               | 1.03               | 0.21       | 0.054      | 0.40                |
| MgO    | 0.024         | 0.13               | 0.078              | 0.11       | 0.004      | 0.058               |
| Na₂O   | 0.015         | 0.03               | 0.020              | 0.024      | 0.018      | 0.037               |
| K₂O    | 0.020         | 0.032              | 0.031              | 0.043      | 0.027      | 0.055               |
| MnO    | 0.01          | 0.001              | 0.015              | 0.010      | 0.011      | 0.013               |
| BaO    | 65.23         | 65.33              | 65.28              | 65.29      | 65.22      | 64.16               |
| SO₃    | 34.13         | 33.97              | 33.19              | 33.58      | 33.92      | 33.10               |
| SrO    | 0.010         | 0.010              | 0.012              | 0.002      | 0.01       | 0.19                |
| LOI    | 0.10          | 0.13               | 0.10               | 0.42       | 0.40       | 0.20                |
The chemical analysis results (Table 4) further aided in calculating the weight per cent composition of BaSO$_4$ (Figure 13) in each of the samples, as shown below. The %BaSO$_4$ composition and other oxides like silica and iron in the samples, compared with the XRD analytical report and the presented SGs, indicated the grade of each baryte sample. Calculation of %BaSO$_4$ in a sample was done following (1) and (2):

(1) \[ \text{BaSO}_4 = \text{BaO} + \text{SO}_3 \]

Where, Molecular Weight: \[ 233.39 = 153.33 + 80.06 \]

(2) Weight% BaSO$_4$ in any Sample X with a given weight %BaO is: \[ \% \text{BaO} \times \frac{233.39}{153.33} \]

Therefore %BaSO$_4$ in the Alifokpa Sample e.g. is: \[ 65.23\% \times \frac{233.39}{153.33} = 99.29\% \]

Figure 13. Weight% concentration of BaSO$_4$ in the Northern Cross River baryte samples.

The analytical results of Northern Cross River samples were highly impressive. Integrating the various results highlighted the bottom line: their suitability for use as a weighting material in drilling muds. The hand specimens from fieldwork showed clean, transparent, tabular barytes, though some had a few inclusions and various colour tints. The Okumurukhtet (Obubra) baryte was immaculate white, ‘sugar baryte’; though associated with galena as revealed by the XRD, quartz and garnets were also observed in this field. The Alifokpa and Gabu 2 mines barytes similarly had associated galena and antimony gangues, though XRD portions did not reveal this fact. Beneficiating the barytes will be a simple mechanical task, as baryte is the primary mineral.

The SG, which is the essential characteristic (McRae, 2016), for all the samples, fell above the API minimum 90% BaSO$_4$. The SGs tests done between (4.37 and 4.52) in two separate and independent laboratories using the API 2004 prescribed Le Chatelier Method (Table 2). All the pulverised samples passed through a 75 µm screen, used for determination of particle sizes, which yielded results: <6 µm and >75 µm, within normal ranges (<30% max and <3% max respectively). The Alkaline earth metals as calcium, in all samples, ranged between 8.40mg/kg and 62.10mg/kg against the 250mg/kg maximum prescribed by API were within an acceptable threshold. Additionally, the pH tests values were all neutral (7). The XRD analysis identified all the samples as baryte with maximum peaks. Only the XRD for the Okumurukhtet (Obubra) sample revealed the presence of an additional mineral, galena, even though galena was also physically present in the Alifokpa baryte mine and is associated with some parts of Gabu. Generally, the chemical analysis on the examined parts of Northern Cross River Barytes presents very high-grade barytes with a good composition of BaO of over 65% and SO$_3$ of about 33.10% - 34.13%. The overall weight percentage of BaSO$_4$ composition ranged between 97.66% and 99.37%, which are also above the API expected minimum limit of 90% (Al-Awad and Al-Qasabi, 2000; Mineral Galleries, 2001; Johnson et al., 2017).
Conclusion
This research evaluated the quality of Nigeria’s Northern Cross River baryte ores for oilfield drilling. It was predicated on the presumption that Nigerian barytes do not meet the API standard for drilling fluid weighting, resulting in massive importation of commercial baryte, causing enormous capital flight and other lost benefits against the country. Fieldwork confirmed the presence of deposits with very impressive weights, various colours, good cleavage and some tabular forms characteristic of very good barytes. In the laboratory, the flame tests and XRD mineralogy integrated with XRF findings confirmed that the samples were excellent quality barytes, with 97.66% to 99.37% BaSO₄ content, which is higher than the 90% prescribed by API for drilling grade baryte. The baryte of various colours tested had no significant impurities of threat or deleterious materials to drilling. Galena was noted as gangue with baryte, especially at Okumurukhet – Obubra, Alifokpa and parts of Gabu but could be easily beneficiated by physical separation, leaving high-quality baryte for drilling and other purposes. The SG of samples, being the most crucial requirement, was authenticated by two separate, autonomous laboratories ranging from 4.37 to 4.52, well above the 4.1 and 4.2 API threshold for oilfield drilling baryte. All other requirements, such as the alkaline earth metals as calcium, Ca, and the particle sizes, specially prescribed by API tests for Drilling Fluid materials, were all within acceptable limits. Therefore, the studied baryte ores meet and exceed the minimum API Standard (API 2004 and 2010) requirements for drilling purposes; and are highly recommended for exploitation in Nigerian oilfields and beyond. Further research, including proper estimation of reserves, is also highly recommended.

This work faced challenges bordering security, general logistics, lack and cost of laboratories and equipment, disorganised and constant abandonment of mines, with adverse environmental impacts, among others. However, these challenges could be resolved or minimised by implementing sound policies in place. With these, the Northern Cross River baryte fields could contribute immensely to a sustainable local supply of API grade baryte for the Nigerian oil and gas industry.

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