Physico-Chemistry of Azara Barytes and its Suitability for Industrial Applications

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Abstract
Azara baryte was subjected to analysis, revealing an average specific gravity of 4.3 g/cm³ and a loss on ignition of 1.71 wt%. The contents of Fe_2O_3, Al_2O_3, and BaO were determined using atomic absorption spectrometry. Gravimetric methods were employed to measure SiO_2 and SO_3, while flame photometry was utilized for the determination of CaO, MgO, Na_2O, and K_2O. The average percentage values for the chemical oxides in the baryte samples were as follows: BaO (57.29 wt%), SO_3 (25.99 wt%), CaO (1.40 wt%), MgO (0.40 wt%), Fe_2O_3 (3.46 wt%), Al_2O_3 (0.97 wt%), Na_2O (2.82 wt%), K_2O (0.30 wt%), and SiO_2 (6.23 wt%). These findings indicate that Azara baryte meets the requirements for use in glass production and as a filler or extender in paint and rubber production. However, further beneficiation is necessary for it to be suitable as a component of oil drilling mud.

Keywords: *Azara Baryte, Specific gravity, Gravimetery, Atomic Absorption Spectrometry, Flame photometry.*

INTRODUCTION

Baryte, also known as heavy spar, is the naturally occurring mineral form of barium sulfate ($BaSO_4$). This mineral is characteristically soft and typically exhibits a clear white color. However, the presence of impurities such as iron oxides, hydroxides, sulfides, and organic matter can cause variations in color, resulting in hues of yellow, blue, red, or even rendering it colorless (Mills & Loving, 1982; Deer, Howie, & Zussman, 1992).

Baryte is notable for its relatively high specific gravity, which ranges from 4.3 to 4.5 g/cm³ (Scott, 1991). This high density makes it valuable in various industrial applications, particularly as a weighting agent in drilling fluids for oil and gas exploration (Blatt *et al.,* 2006). The mineral also has a refractive index of 1.63, contributing to its use in optical applications (Anthony *et al.,* 2001).

Structurally, baryte crystallizes in the orthorhombic system, a feature that influences its cleavage and physical properties (Berry, Mason, & Dietrich, 1983). Furthermore, baryte is characterized by its very low solubility in water, making it stable in a wide range of environments (Leach & Sangster, 1993). It is non-toxic and remains chemically and physically unreactive under normal conditions, which further enhances its desirability for use in various industries, including medical imaging, paint, and plastics (Roskill Information Services, 2006; Wood, 2005; Mathew, *et al.*, 1971).

Baryte commonly occurs as a gangue mineral within lead and zinc sulfide veins hosted in limestone formations (Petrucci *et al.,* 2002). It is also found in association with hematite ore and as precipitates in hot spring environments (Deer *et al.,* 1992). Common mineral associates of baryte include anglesite and celestine (Klein and Hurlbut, 1993). The term “primary baryte” refers to the first marketable product which include crude baryte and the product of simple beneficiation methods such as washing, jiggling, heavy media separation, tabling, flotation and magnetic separation.

About 80% of world produced barytes are used in the oil well drilling mud as “heavy mud”. They also find extensive use as source raw material for barium compounds such as $BaCl_2$ and $Ba(NO_3)_2$. Ground baryte is used as filler in the manufacture of linoleum, oil cloth, paper, textile, rubber and plastic manufacturing. Prime white, a bleached baryte is used as a pigment in white paint, but not as satisfactory as Blanc fix, or chemically precipitated $BaSO_4$ or lithopone, a mixture of $BaSO_4$ and ZnO. Baryte gives greater brilliance in glass due to its brilliant appearance. From environmental point of view baryte has a strong inertia, good stability, acid and alkali proof, moderate rigidity, high specific gravity, high absorption of harmful radiation and is practically insoluble under ordinary conditions in all the usual chemical solvents.

In Nigeria, baryte deposits can be found in Azara, Gbande, Aloshi, Akin and Keana all scattered within Nassarawa and Plateau States. Deposits are also found in Lefin in Cross River State and Ibi and Dungel in Taraba State. Smith (1978) estimated that the Azara baryte deposit has a proven reserve of about 731,000 tonnes with about 71,000 tonnes of good quality barytes.

Global barytes production in 2020 was estimated at 12 million metric tons (USGS, 2021). Approximately 88% of this output was consumed by the oil and gas sector as a crucial additive in drilling fluids (Grand View Research, 2023). As a result, the barytes market exhibits a strong correlation with oil industry activities.

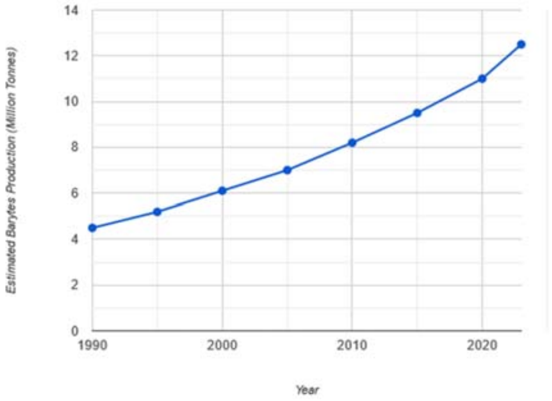

Figure 1: Estimated Global Barytes Production over the years

The Nigerian oil and gas industry is solely dependent on imported baryte but with the current drive in the oil and gas industry local content policy of government, it becomes necessary to assess the in to quality of the Azara deposit. The characterization of the Azara baryte to ascertain its main constituents and possible suitability as a local baryte source in the formulation of oil drilling mud (heavy mud) for the oil and gas industry will go a long way in achieving this main objective of the government in that sector.

Geography and Geology of Deposit

The Azara baryte deposit is located at about 98km south of Lafia the capital of Nasarawa State. 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 70º, while others are at an angle of 45º. The over burden on the veins varies 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.

MATERIALS AND METHODS

The baryte samples were collected from Azara in Azara Local Government Area of Nassarawa State. Three different samples in lump sizes were collected each from a vein in the deposit with the aid of diggers and shovels. The collected samples were then placed in polythene bags and sealed to prevent loss of moisture.

The preparation of samples and analysis were carried out at the National Geosciences Research Laboratory Centre (Geological Survey Agency), Kaduna. Each sample was first crushed manually with a hammer into large fragments before being subjected to further crushing into smaller particle size fractions using a Jurgen and Bremen jaw crushers' respectively. Thus, to obtain greater proportions of grain particle sizes of less than 1cm the crushing was repeated two times. Finally, the samples were further pulverized to get a fine powder in a porcelain ball mill with balls (Chesters, 1973 and Chesti, 1994). The powder obtained was separately sieved through a 100 mesh size and packed in polythene bags.

The physical analyses carried out were the specific gravity and loss on ignition, while the chemical analyses include the use of atomic absorption spectrometer and flame photometer to determine BaO, Cao, Fe_2O_3, MnO, TiO_2, Al_2O_3, Na_2O, K_2O and gravimetric method to determine SiO_2 and SiO_3.

The sample preparation was carried out as described by Van Loon (1996). Pye Unican 929 Atomic absorption spectrometry and Model FP 6410 flame photometer were used for the metal analyses

Loss on Ignition (LOI)

A gramme of the sample was weighed into a porcelain crucible. The crucible was then placed in a muffle furnace and the temperature was gradually increased from 320ºC to 1000ºC and maintained for 2 hours. The crucible was removed, allowed to cool further in a desiccator and weighed. The crucible was returned to the furnace at 1000ºC for another 10 minutes and then reweighed. This procedure was repeated until a constant weight was obtained (Rowell, 1994). The L.O.I. was calculated using equation (1):

$$LOI = \frac{M - m}{M} x\ 100 \ldots\ldots\ldots\ldots\ldots (1)$$

where: M = mass of sample (g) and m = mass of sample after ignition (g)

Specific Gravity

An already prepared pycnometer bottle was weighed and filled to $^{1}/_{3}$ its volume with the sample, reweighed. This is followed by weighing the pycnometer plus sample and water and finally by taking the weight of the pycnometer and water. This procedure was carried out for each of the three samples.
The specific gravity was calculated as:

True specific gravity =

$$\frac{weight\ of\ sample}{weight\ of\ an\ equal\ volume\ of\ water} \cdots\cdots\cdots (2)$$

$$\therefore \text{ True specific gravity} = \frac{b-a}{(b+d)-(a+c)}$$

where:
a = weight of empty pycnometer bottle
b = weight of pycnometer + sample 1/3 of the bottle capacity
c = weight of pycnometer + sample + water
d = weight of pycnometer + water

Determination of Ba, Al, Ti, Fe, and Mn Using AAS Model 929

A fresh gramme of the ground sample was weighed and placed into a platinum crucible, mixed with 2g Na_2CO_3 and 0.3g KNO_3.The mixture was fused at 1000°C for 30 mins in a furnace. The fused product was extracted with dilute 1M HCl. The Silica content was filtered and determined gravimetrically. From the filtrate, Fe and Mn were determined using Air/Acetylene, while Ba, Al, and Ti were determined using N_2O/Acetylene. A blank solution was prepared by the same procedure excluding the sample. The blank solution was used to remove the effect of the reagents used for the preparation of the sample on the absorbance of the elements to be determined. 1-10µg/cm^3 solutions of Ba, Al, Ti, Fe, and Mn were prepared from their respective salts and used for calibration. The metal concentrations were determined by interpolation using the calibration curve. The metal oxide was determined from the expression:

$$\text{Metal oxide (\%)} = \frac{x}{y} \text{ x Mwt x } 100$$

where: x = amount of metal in mg x 10^{-3}
y = atomic mass of the metal
Mwt = molecular mass of the metal oxide

The SO_3 content was determined gravimetrically (Belcher and Freiser, 1956).

Determination of Na, K, Ca and Mg Using Flame Photometer Model FP 6410:

A fresh gramme sample was taken and digested with conc. HF and conc. H_2SO_4. The solution was filtered and the filtrate used for the determination of the elements.

RESULTS AND DISCUSSIONS

Table 1: Percentage Oxide Composition for Azara Baryte Samples

Major oxides	Percentage compositions				Standard Deviation
	A	B	C	Average	
BaO	60.70	5670	54.46	57.29	3.16
SO_3	27.10	23.37	27.50	25.99	2.28
CaO	1.40	2.80	ND	2.10	1.40
MgO	1.20	ND	ND	1.20	0.60
SiO_2	4.20	7.20	7.30	6.23	1.761
Fe_2O_3	0.79	5.10	4.50	3.46	2.334
MnO	TR	TR	TR	TR	0.000
TiO_2	TR	TR	TR	TR	0.000
Al_2O_3	0.53	0.78	1.60	0.97	0.600
Na_2O	2.62	2.54	3.31	2.82	0.423
K_2O	0.24	0.18	0.48	0.30	0.158
H_2O^+	2.15	1.28	1.69	1.71	0.450
S.G.	4.48	4.43	4.38	4.43	0.050

The provided Table 1, presents the percentage oxide composition, standard deviation, and specific gravity (S.G.) data for three Azara baryte samples labeled A, B, and C, along with the average values. Baryte, chiefly composed of barium sulfate ($BaSO_4$), is a mineral with substantial industrial significance. Its fitness for various applications hinges on its purity, which is often expressed in terms of its oxide composition (Krauskopf & Bird, 2009).

Barium Oxide (BaO): The BaO content across the samples ranges from 54.46% (sample C) to 60.70% (sample A), with an average of 57.29%. Theoretically, pure $BaSO_4$ contains 65.7% BaO. The lower BaO values in these samples suggest the presence of impurities such as silica (SiO_2), iron oxide (Fe_2O_3), and alumina (Al_2O_3) (Meinert *et al.,* 2016).

Sulfur Trioxide (SO_3): The SO_3 content varies from 23.37% (sample B) to 27.50% (sample C), with an average of 25.99%. This range aligns with the BaO variations, as both elements originate from the sulfate (SO_4) component of $BaSO_4$.

Calcium Oxide (CaO): The CaO content shows variation, with values of 1.40% (sample A) and 2.80% (sample B), and is absent (ND) in samples C. The presence of CaO indicates the possible presence of mineral impurities like calcite ($CaCO_3$) (Hodge & Smith, 1941).

Magnesium Oxide (MgO): MgO is only detected in sample A (1.20%) and is absent (ND) in samples B and C. The presence of MgO suggests possible mineral impurities like dolomite ($CaMgCO_3$) (Hodge & Smith, 1941).

Silicon Dioxide (SiO_2): The SiO_2 content ranges from 4.20% (sample A) to 7.30% (sample B), with an average of 6.23%. Elevated SiO_2 content can reduce the specific gravity of baryte, making it less desirable for applications like oil well drilling fluids (Speight, 2010).

Iron Oxide (Fe_2O_3): The Fe_2O_3 content varies from 0.79% (sample A) to 5.10% (sample B), with an average of 3.46%. High Fe_2O_3 content can impart color to the baryte, affecting its suitability for pigment production (Nesbitt & Young, 1989).

Aluminum Oxide (Al_2O_3): The Al_2O_3 content shows some variation, ranging from 0.53% (sample A) to 1.60% (sample C), with an average of 0.97%. The presence of Al_2O_3 suggests possible mineral impurities like clays (Deer *et al.,* 2013).

Other Oxides: Minor quantities of Na_2O, K_2O, MnO, and TiO_2 are also present in the samples. These elements may be associated with trace minerals within the baryte deposit.

Specific Gravity (S.G.): The S.G. values range from 4.38 (sample C) to 4.48 (sample A), with an average of 4.43. Generally, baryte has a specific gravity of around 4.5 (Meinert *et al.,* 2016). The slightly lower S.G. values in these samples could be due to the presence of lighter impurities like silica.

Table 2: Chemical Oxide Content of Azara Baryte Sample Compared with Standared Baryte Composition.

Oxide Composition	Azara Baryte	*Standard Grade Baryte Powder
$BaSO_4$	83.28wt%	96.00wt%
$CaSO_4$	1.40wt%	0.60wt%
SiO_2	6.23wt%	3.50wt%
Fe_2O_3	3.46wt%	0.05wt%
Specific Gravity	4.43	4.30

Table 2 presents a comparative analysis of the oxide composition of Azara baryte and a standard grade baryte powder.

BaSO4 Content: The most striking disparity lies in the $BaSO_4$ content, the primary mineral constituent of baryte. While standard grade baryte boasts a $BaSO_4$ content of 96.00 wt%, the Azara sample falls significantly short at 83.28 wt%. This substantial difference underscores the lower purity of the Azara baryte and consequently limits its applicability in industries demanding high-purity barium sulfate.

Impurity Levels: The elevated levels of impurities, such as SiO_2 (6.23 wt%) and Fe_2O_3 (3.46 wt%) in the Azara baryte compared to the standard limits of 3.50 wt% and 0.05 wt%, respectively, further exacerbate its quality. These impurities can adversely affect the physical properties and color of the baryte, rendering it unsuitable for applications requiring high-purity and whiteness.

Specific Gravity: While the specific gravity of the Azara baryte (4.43) is marginally higher than the standard value (4.30), this slight increase is insufficient to compensate for the significant deficiencies in $BaSO_4$ content and impurity levels.

Implications for Industrial Applications

The oxide composition data indicates that the Azara baryte samples contain impurities that may affect their suitability for various applications. However, some potential implications can be found in:

Oil Well Drilling Fluids: The elevated levels of SiO_2 in some samples (exceeding 4%) could make them less suitable for oil well drilling fluids, where high specific gravity is desirable (Speight, 2010).

Pigments: The Fe_2O_3 content can affect the color of the baryte, potentially impacting its use in pigment production. However, the Fe_2O_3 levels in these samples might be acceptable depending on the desired color and application (Nesbitt & Young, 1999)

The aforementioned compositional disparities restrict the applicability of Azara baryte to high-value industrial sectors such as oil and gas, paints, and rubber. However, with appropriate beneficiation processes to remove impurities and concentrate the $BaSO_4$ content, the Azara baryte may find utility in lower-grade applications, such as fillers or extenders in paper and construction materials.

CONCLUSION

The chemical analysis of the Azara baryte sample highlights its inferior quality compared to standard grade baryte. To enhance its commercial value and expand its application range, significant beneficiation efforts are required to improve the $BaSO_4$ content and reduce impurity levels. Further investigations into the mineralogical composition and the geological setting of the Azara deposit could provide valuable insights into the formation of the baryte and potential strategies for its upgrading.

RECOMMENDATIONS

From the results obtained for the analysis of Azara barytes the following recommendation may be made:

1. Azara barites will have to undergo further beneficiation in order to improve on its percentage $BaSO_4$ content from 83.28wt% to the minimum of 96wt% which is required for oil drilling mud.
2. Further beneficiation of Azara baryte is likely to reduce its present high Fe_2O_3content thereby improving its white rate from the present grey colour.
3. Azara baryte if improved to 96wt% $BaSO_4$ and a minimum white rate of 88% will be a suitable substitute in oil drilling mud formulation and will be readily available for other applications.

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