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Research Article

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Characterization of Baryte from Torkula and Kaseyo of Guma Local Government Area, Benue State, Nigeria

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1. Introduction

It was in view of the ever-increasing cost of imported raw materials and the continuous demand for baryte in Nigeria's fast growing oil and gas industry, that the Nigerian government-imposed ban on the importation of such materials and encouraged local production. It has then become imperative to focus attention on the neglected exploration and exploitation of baryte deposits abound in Nigeria. The occurrence of baryte in parts of the Middle Benue Trough was first reported by Tate (1959) in his memorandum, Geological Survey of Nigeria Report No.

1266 and he estimated the reserve to be about 400,800 tons to 18 (m) depth. Baryte, a translucent white to grey-black, heavy and inert mineral is the naturally occurring form of barium sulphate (BaSO₄). Because of the high specific gravity of baryte, nearly three quarters of the domestic output of the mineral is used in oil industry as drilling fluids. Baryte has numerous other uses, such as in the manufacture of glass and white pigment as a filler or extender in paints, ink soil-cloth, and in the manufacture of barium compounds for industrial applications. From the above demand this work is aimed at furthering the exploration of the baryte mineral deposit of

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ABSTRACT

Samples from the baryte mineral deposit at Torkula and Kaseyo of Guma local government area, Benue, Nigeria were analyzed for their physical, chemical and mineralogical properties, such as hardness, specific gravity etc. The elemental composition was determined by the use of X-ray Fluorescence (XRF) and mineralogical analysis was done by the use of X-ray powder diffraction (XRD). The chemical analytical results indicate the following range of values for the oxides; SiO₂ (15.55% - 15.60%), Fe₂O₃ (0.27% - 0.29%), BaO (71.46% - 70.87%), TiO₂ (1.60 % - 1.58%), CaO (0.09% - 0.10%), P₂O₅ (0.01% - 0.01%), K₂O (0.03% - 0.04%), MnO (0.06% - 0.05%), MgO (0.03% - 0.04%), Na2O (0.07% - 0.07%), Cu2O (0.05% - 0.06%), RbO (0.07% - 0.06%), ZrO (0.08%), Cr₂O₃ (0.1% - 0.12%), Al₂O₃ (1.31% - 1.28%). The mineralogical analysis shows the presence of calcite, albite, hematite, quartz, kaolinite and montmorillonite. Quartz and kaolinite were predominant. The baryte from both Torkula and Kaseyo were considered good grade for use as drilling mud when compared with the American Petroleum Institute (API) standards. They also compare reasonably well with the American Society for Testing and Materials (ASTM) standard for applications in glass, pharmaceuticals, paint and chemical production. However, the baryte will require a beneficiation process to reduce the concentration of the silica (SiO₂) content.

Torkula and Kaseyo in Guma local government area of Benue State, and to also analyse and process the samples collected in order to ascertain the quality when compared with international standards.

2. Geology of the Study Area

The study area (Torkula and Kaseyo) is located at Guma Local Government Area of Benue State. It is accessible only

by means of foot, motorcycles or large trucks due to the very poor nature of the roads.

The study area is part of the Middle Benue Trough of Nigeria (Fig. 1) and composed of the Late Albian - Cenomanian, Awe and Keana Formations (consisting essentially of sandstones with intercalations of bands of shales and clays) and Cenozoic Volcanics (Fig. 2).



Fig. 1. Geological map of Nigeria showing study area. (After Obaje, 2009)

The Middle Benue Trough extends Northeast ward approximately as far as line joining Bashar and Mutum Biyu. This boundary marks the Southern limit of the Gombe and Keri-Keri Formation while the older sediments of the Upper Benue Trough undergo lateral facies change in this area (Fig. 2). The Middle Benue Trough is relatively poorly known, especially in its Northeastern part; no detailed geological maps of this portion are available but the area immediately south of Bashar was included in a photo-geological map. Maps of the Lafia-Keana-Awe region were presented by Offodile (1976) and Offodile and Reyment (1977).

3. Materials and Methods

Ore deposits (Hydrothermal vein deposits) were mapped out in Torkula and Kaseyo and fresh samples collected with the aid of a sledge hammer and properly labelled were sent to the laboratory for analysis. At the laboratory, the baryte samples were pulverized into smaller pieces until the fine powdered form was obtained. The powdered baryte was poured into a ndicott mesh sieve size of 250 microns to produce finer particles which is the grain size distribution of the modified baryte sample. The powdered sample was stored in an air tight container prior to testing.

3.1. Geotechnical analysis

Various tests were conducted such as hardness using finger nail to scratch the sample and calcite as a reference point because of its known hardness. Tenacity of the baryte sample was determined by putting the sample in a sack bag and kept on an anvil, where it was then hit once with a hammer, thereby shattering. Specific gravity which is the ratio of density of the solid to density of water at a stated temperature, was also determined.

3.2. XRF analysis

XRF analysis was conducted to determine the chemical composition of the samples. However, the process involved crushing of each sample block with an electric crusher and then pulverizing the pieces for 60 seconds using Herzog Gyro-mill (Simatic C7-621). Thereafter, pellets were prepared from the pulverized sample, first by grinding 20g of each sample with 0.4g of stearic acid for 60 seconds. 1g of stearic acid was weighed into an aluminum cup to act as binding agent and the cup was subsequently filled with the sample to the level point. The cup then taken to Herzog pelletizing equipment when it was passed at a pressure of 200KN for 60 seconds. The 2mm pellets were then transferred into a sample holder of the X-Ray equipment (Phillips PW-66) for analysis.

3.3. XRD analysis

In order to obtain a diffraction pattern of the mineral, 2 grams of the coarse particles were transferred to the steel container, then the "Little Smasher" was used to reduce the size of larger chips to approximately sand-size (less than 1 or 2 mm), in the Spex Mixer. The grinding container was mount onto the mixer, fastened snugly, and the lid closed. The mixer was turned on for at least 5 minutes. After grinding is complete, the powder form was transferred into a piece of weighing paper and then sieved through the 270-mesh sieve to obtain a finer form which was thereafter introduced into a sample holder of the X-Ray equipment for analysis.

4. Results and Interpretation

From Table 1, the SiO₂ concentration in both samples ranged between (15.55 - 15.60)%. This is due to the ubiquitous nature of quartz and also due to the occurrence of the hydrothermal deposits in quartz-rich shale and sandstone. The barium (BaO) concentration in both analyzed samples exceeds 70% and water-soluble alkaline earth metals such as calcium is less than 0.25% making the baryte of very good quality.



Fig. 2. Geological map of the study area

From the result of the analysis presented in Table 2, it was observed that the human fingernail could not scratch the barite samples but a copper penny could, thus placing the hardness of the barite between 3 (calcite hardness) and 4

(fluorite hardness). Therefore, the hardness of the sample lies between 3.0-3.5 which meets up to API specification for hardness. They shattered easily on application of external force showing that their tenacity is brittle.

Table 1. Oxide concentration of baryte samples

Oxides Concentration (%)	Torkula sample	Kaseyo sample
BaO	71.46	70.87
SiO ₂	15.55	15.60
Al ₂ O ₃	1.31	1.28
Fe ₂ O ₃	0.27	0.29
TiO ₂	1.60	1.58
CaO	0.09	0.10
P_2O_5	0.01	0.01
K ₂ O	0.03	0.04
MnO	0.06	0.05
MgO	0.03	0.04
Na ₂ O	0.07	0.07
Cu ₂ O	0.05	0.06
ZnO	ND	ND
RbO	0.07	0.06
ZrO	ND	0.08
Cr_2O_3	0.1	0.12
LOI (Loss on Ignition)	8.04	8.05
Total	98	98

ND: Not Detected

Table 2. Result of hardness test carried out on the samples

No	Sample Location	Sample color	Streak	Sample hardness	API standard hardness
1	Torkula	White	White	3.0 - 3.5	3.0 - 3.5
2	Kaseyo	White	White	3.0 - 3.5	3.0 - 3.5

Results (Table 3) of the specific gravity test shows that the baryte from both locations meets up to API specification for specific gravity.

The XRD analysis is semi quantitative based on the fact that the peak height in the diffractogram is proportional to the concentration of the mineral in the sample.

Samples	Torkula	Kaseyo
W1 (g): Weight of empty density bottle	26.90	26.00
W2 (g): Weight of density bottle + Kerosene	66.90	66.00
W3 (g): Weight of density 25g of baryte powder	51.90	51.00
W4 (g): Weight of density bottle + Kerosene + 25g baryte	87.10	86.41
W5 (g): weight of density bottle + water	75.59	75.50
Specific Gravity	4.28	4.47
API Specific Gravity	4.2	4.2

The high-score spectral analysis software of the XRD automatically detected the quartz mineral to peak in all the samples. This is because quartz is by far the most common of the silica minerals in the sedimentary rocks and its diffraction lines can be used as internal standard for the accurate and precise measurement for the inter-planar spacing (d in Å) (Moore and Reynolds, 1989). From the analysis of sample 1 (Fig. 3), the quartz peak at 9.26Å (25.45, 20) with 100% intensity was found to be the highest peak. Other quartz peaks are 4.26Å (14.55, 20) (55%), 3.33Å (27.01, 20) (40%) and 1.45Å (50.46, 20) (20%).



Fig. 3. Peak values for Sample 1 (Torkula)

The next highest peak from quartz (9.26Å) was the peak at 5.34Å, which was the 70 % intensity peak of baryte. Other baryte peaks were also found at 5.34Å (15.2, 2 θ) (60%) and 1.77Å (45.37, 2 θ) (30%). After the quartz and baryte peaks had been sorted out, the next highest peaks were found at 3.35Å d-spacing position, which was identified as the

kaolinite with 50% intensity. The peak at 7.22Å was also kaolinite with 40% intensity. In the same way the calcite peak was found at 1.72Å (28.12, 2 θ) (30%).

Albite peaks were found at 1.97Å (36.01, 2 θ) (20%) and 1.97Å (40.12, 2 θ) (30%). The montmorillonite peak was

found at 1.44Å (10.33, 2 θ) (30%) and hematite peak was found at 1.34Å (85.33, 2 θ) (24%).

From the analysis of sample 2 (Fig. 4), the quartz and kaolinite peaks at 9.26Å and 7.29 Å respectively were found to be the highest peaks. The quartz peaks are 9.26Å (14.22, 20) 100% intensity, 3.33Å (28.22, 20) (35%) and 1.78Å (62.66, 20) (30%). The kaolinite peaks were found at 7.29Å (30.13, 20) (100%) and 3.35Å (37.22, 20) (40%). The next

highest peak after quartz and kaolinite was the baryte peak at 5.34\AA (31.345, 20) with 70% intensity.

Other baryte peaks were found at 5.21Å (20.14, 2 θ) (40%), 3.97Å (44.13, 2 θ) (30%) and 1.76Å (45.24, 2 θ) (22%). The hematite peak was found at 4.24Å (58.27, 2 θ) (40%). The montmorillonite peak was found at 1.44Å (67.35, 2 θ) (30%). The albite peak was found at 1.77 Å (54.18, 2 θ) (25%). The calcite peak was found at 1.57 Å (64.45, 2 θ) (20%).



Fig. 4. Peak values for Sample 2 (Kaseyo)

The barytes sampled in the field were found as veins cutting through the parent rocks; shale, siltstone and sandstone, vertically. And it is in association with other minerals such as galena (Fig. 5). The observed contact between the vein and the host rock is sharp with absence of wall-rock alteration.



Fig. 5. Baryte vein (green pen) and associated mineral galena (blue pen)

From the peak values of the XRD analysis (Figs. 2 and 3) of samples from both locations, quartz was detected as the highest peak making it the most common impurities in the

samples which can easily be separated by gravity. The presence of low temperature minerals such as quartz in baryte coupled with the coarse-grained texture of the baryte predicts a probable correlation of the process of formation of the baryte to low temperature (Offodile, 1976, Tanko et al., 2015). The invariable association of baryte with quartz, suggest that the baryte veins of the studied area appear to have been formed during the later stage of the Cretaceous (Offodile, 1976, Tanko et al., 2015).

The presence of the minerals (calcite, albite, hematite, quartz, kaolinite and montmorillonite) is because of the association and occurrence of barite in silicate carbonate rocks and siltstone-sandstone sequences (Cronan, 1969). And also, baryte occurrence has been found to be in low-temperature hydrothermal veins; in residual deposits from weathered baryte-bearing limestone; as an accessory mineral in igneous rocks; in carbonatites; a primary component of submarine volcanogenic massive sulphide deposits and sea-floor chimneys. The dominant impurities from both samples are quartz and kaolinite which correlates the occurrence and association of the barytes to silicate carbonate rocks. Fe₂O₃ and SiO₂ act as contaminants in baryte ore which reduces its specific gravity and also affect its colour and brightness. Purer baryte range from colourless to white in colour and have a brighter appearance. Barytes from both locations are white and high in brightness making them useful in the paint and medical industries.

There are various industrial specifications for different uses of baryte. Therefore, a comparison of the analyzed geotechnical and geochemical properties with some generally acceptable standards (Table 4) for processed baryte was done as there are no standards for mineral ore. From the comparison, it is seen that the ore samples from both locations compare reasonably well with the API specification standard for baryte used as a weighting agent in oil well drilling mud (specific gravity of 4.2 min).

Also, the water-soluble element CaO (0.09% - 0.10%), of both locations, is low in concentration indicating good grade baryte for drilling mud. The concentrations of Al₂O₃ (1.31% - 1.28%), SiO₂ (15.55% - 15.60%) and Fe₂O₃ (0.27% - 0.29%) from both locations, indicate that the barytes will require a

beneficiation process to reduce the concentrations in order to be suitable for use in glass; glass and pharmaceuticals; paint, glass, and chemical production; respectively, as compared with the ASTM.

The results correlate well as compared with analysis from selected localities in Nigeria (Table 5) which shows that barytes from the study area is averagely low in concentrations of Al₂O₃, Fe₂O₃, CaO, and MgO. However, Oden (2012) noted that in the Benue trough the quality of baryte increases with depth of the veins. He observed that in most occurrences, the quality of the material from top part of a vein (0 - 5 m depth) is always lower than that from the deeper parts of the same vein. Therefore, as mining gets deeper in the study area better quality of baryte could be acquired.

Table 4. General specification standards for various uses of baryte ores (Ene et al., 2012)

Standard	Specific Gravity	BaSO4	Soluble alkaline content (Sr and Ca)	Heavy metals	Fe2O3	SiO ₂	Al ₂ O ₃	Moisture Content
API (Drilling mud)	4.2 (min)	92 % (min)	250 ppm max	N/A	N/A	N/A	N/A	N/A
Glass	N/A	95 % (min)	N/A	N/A	1.5% (max)	1.5% (max)	1.5% (max)	N/A
Pharmaceuticals	N/A	97.5 % (min)	<0.01 ppm	<0.01 ppm (max)	N/A	1.5 % (max)	N/A	N/A
Paint	N/A	95 % (min)	0.2 % (max)	N/A	0.05 % (max)	N/A	N/A	0.5 % (max)
Chemicals	N/A	92 % (min)	1 % (max)	N/A	1 % (max)	N/A	N/A	N/A

Table 5. A brief comparison of baryte composition from different localities in Nigeria

	Middle Benue Trough				Lower Benue Trough		Sokoto Basin	
Oxides Concentration	Study Area		Azara 1	Azara 2	Gabu	Alifokpa	Bukkuvum LGA	
•••••••	1 (Torkula)	2 (Kaseyo)	(Isa et al., 2007)	(Isa et al., 2007)	(Ene et al., 2012)	(Ene et al., 2012)	(Olusegun et al., 2015)	
BaO	71.46	70.87	89.88	65.02	75.54	74.87	71.46	
SiO ₂	15.55	15.60	9.31	0.029	1.38	0.07	4.55	
Al ₂ O ₃	1.31	1.28	0.62	16.62	0.43	0.52	1.31	
Fe ₂ O ₃	0.27	0.29	0.028	18.12	8.06	10.53	0.27	
TiO ₂	1.60	1.58	-	-	-	-	1.60	
CaO	0.09	0.10	0.014	0.006	0.01	0.02	0.09	
P2O5	0.01	0.01	-	-	-	-	-	
K ₂ O	0.03	0.04	0.015	0.001	-	-	0.06	
MnO	0.06	0.05			-	-	0.01	
MgO	0.03	0.04	0.04	0.024	-	-	0.03	
Na ₂ O	0.07	0.07	0.025	0.028	-	-	0.07	
Cu ₂ O	0.05	0.06	-	-	-	-		
ZnO	ND	ND	-	-	-	-	-	
RbO	0.07	0.06	-	-	-	-	-	
ZrO	ND	0.08	-	-	-	-	-	
Cr2O3	0.1	0.12	-	-		-	-	
LOI	8.04	8.05	0.06	0.044	-	-	1.05	
TOTAL	98	98	-	-	-	-		

ND: Not Detected; LOI: Loss on ignition

5. Conclusion

The results of mineralogical analysis, oxide concentration, tenacity, hardness and specific gravity tests carried out show that the local baryte from Torkula and Kaseyo are of good grade, good quality and meet up to API standard for baryte as a drilling mud additive.

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