



Chemsearch Journal 1(1): 1 - 3

Received: October, 2009

Accepted: May, 2010

Publication of Chemical Society of Nigeria, Kano Chapter

DETERMINATION OF THE CONSTITUENTS AND SUITABILITY OF AZARA BARYTES FOR INDUSTRIAL APPLICATIONS

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ABSTRACT

Azara baryte was analyzed and had an average specific gravity of 4.3g/cm³ and loss on ignition of 1.71wt%. Atomic Absorption spectrometry was used to determine the Fe₂O₃, Al₂O₃ and BaO contents. SiO₂ and SO₃ were determined by gravimetry while CaO, MgO, Na₂O and K₂O were determined by flame photometry. The percentage average values for the chemical oxides in the baryte samples were BaO (57.29wt%), SO₃(25.99wt%), CaO(1.40wt%), MgO(0.40wt%), Fe₂O₃(3.46wt%), Al₂O₃(0.97wt%), Na₂O(2.82wt%), K₂O(0.30wt%) and SiO₂(6.23wt%). These results indicate that Azara baryte lies within the range for use in glass production and as a filler or extender in paint and rubber production, but will require further beneficiation in order to be a suitable component of oil drill mud.

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

INTRODUCTION

Baryte (heavy spar) is the naturally occurring mineral of barium sulphate (BaSO₄). Baryte is soft with clear white colour, but can vary with the presence of impurities (such as iron oxides, hydroxides, sulphides and organic matter) giving colours such as yellow, blue, red or colourless. It has a relatively high specific gravity of 4.3-4.5g/cm³, a refractive index of 1.63 and an orthorhombic crystal structure. It has a very low solubility, non-toxic, chemically and physically unreactive (Wood, 2005; Mathew, et al. 1971; <http://minerals.usgs.gov/minerals/pubs/commodity/baryte.html>, 2008(a); www.webmineral.com/data/barytes.html, 2008(b)).

Barytes commonly occur in lead and zinc veins in limestone, in hot spring deposits and with hematite ore. It is often associated with the minerals arnglesite and celestine (<http://en.wikipedia.org/wild.baryte>, 2008(c)). The term "primary baryte" refers to the first marketable product which include crude baryte and the product of simple beneficiation methods such as washing, jigging, 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 BaCl₂ and Ba(NO₃)₂ (www.apmines.com/geology/ouddah.htm, 2008(d); www.mineral.it/mineral2/b/baryteenglish.html, 2008(e)). 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 BaSO₄ or lithopone, a mixture of BaSO₄ and ZnO. Baryte gives greater brilliance in glass due to its brilliant appearance (www.mineralzone.com/minerals/barytes.html, 2008(f)).

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, Alosi, Akin and Keana all scattered within Nassarawa and Plateau States. Deposits are Iso

found in Lefin in Cross River State and Ibi and Dungal 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.

The world production of barytes was estimated at 6.3Mtpa in 2004 of which 88% is consumed by the oil and gas industry as an addition to the oil drilling fluids. Thus, the baryte market is very closely tied to the activity in the oil industry (Rivera and Radovic, 2004).

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 objectives 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 dissolve 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.

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

$$LOI = \frac{M - m}{M} \times 100 \dots \dots \dots (1)$$

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:

$$\text{True specific gravity} = \frac{\text{weight of sample}}{\text{weight of an equal volume of water}} \dots \dots \dots (2)$$

$$= \frac{b - a}{(b + d) - (a + c)}$$

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 Na₂CO₃ and 0.3g KNO₃. 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

$$\% \text{ metal oxide} = \frac{x}{y} \times \text{Mwt} \times 100$$

Where: x = amount of metal in mg x 10⁻³
 y = atomic mass of the metal
 Mwt = molecular mass of the metal oxide

The SO₃ 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. H₂SO₄. The solution was filtered and the filtrate used for the determination of the elements.

RESULTS AND DISCUSSION

The results of the analyses of Azara barytes are presented in Tables 1 and 2. The baryte sample had an average loss on ignition of 1.71wt% and an average specific gravity of 4.43. The average oxide values obtained for the three samples were BaO

BaO, Cao, Fe₂O₃, MnO, TiO₂, Al₂O₃, Na₂O, K₂O and gravimetric method to determine SiO₂ and SiO₃.

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 320°C to 1000°C 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 1000°C 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):

using N₂O/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/cm³ 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:

(57.29wt%), SO₃ (25.99wt%), CaO (1.40wt%), MgO (0.40wt%), SiO₂ (6.23wt%), Fe₂O₃ (3.46wt%), Al₂O₃ (0.97wt%), Na₂O (2.82wt%), K₂O (0.30wt%). The specific gravity of 4.43 makes Azara baryte a useful raw material for industrial use when compared to the standard value of 4.30. The 1.71wt% loss on ignition is slightly above the maximum value of 1.0wt% required for oil drilling grade for crude baryte.

The combined BaSO₄ value of 83.28wt% placed Azara baryte well below the minimum value of 96wt% which is required for any industrial application.

The Fe₂O₃ of 3.46wt% is well above the minimum of 0.05wt% required for a good quality baryte of 88% white rate. The iron oxide must have impacted the grey colour on Azara baryte. The SiO₂ content of

6.23wt% almost double the tolerable maximum limit of 3.5wt%. However, it can conveniently be used for the production of sodalime glasses and as filler for low quality papers.

Table 1: Percentage Oxide Composition for Azara Baryte Samples

Major Oxides	Percentage Composition				Average	S.D. = $\frac{\sqrt{(X - \bar{X})}}{N - 1}$
	A	B	C			
BaO	60.70	56.70	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 ₂ O 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 ₂ O ₃	0.53	0.78	1.60	0.97	0.600	
Na ₂ O	2.62	2.54	3.31	2.82	0.423	
K ₂ O	0.24	0.18	0.48	0.30	0.158	
H ₂ O ⁺	2.15	1.28	1.69	1.71	0.450	
S.G.	4.48	4.43	4.38	4.43	0.050	

Table 2: Chemical Oxide Content of Azara Baryte Sample Compared With Standard 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 ₂ O ₃	3.46wt%	0.05wt%
Specific Gravity	4.43	4.30

*www.mineralzone.com/minerals/barytes.html

CONCLUSION

The results of the physiochemical analyses obtained for Azara barytes shows that it can be used as a filler or extender in the rubber and paper industries. However the samples will require further mineral processing in order to conform to the very high quality requirement of the oil and gas industry.

Recommendations

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

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1. Azara barites will have to under go further beneficiation in order to improve on its percentage BaSO₄ 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 Fe₂O₃ content thereby improving its white rate from the present grey colour.
3. Azara baryte if improved to 96wt% BaSO₄ 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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