



BENEFICIATION OF AZARA BARITE ORE USING A COMBINATION OF JIGGING, FROTH FLOTATION AND LEACHING

H. E. Mgbemere^{1,*}, E. O. Obidiegwu² and E. Obareki³

^{1,2,3} DEPT. OF METALLURGICAL AND MATERIALS ENGINEERING, UNIV. OF LAGOS, AKOKA, LAGOS STATE, NIGERIA

E-mail addresses: ¹hmgbemere@unilag.edu.ng, ²eobidiegwu@unilag.edu.ng;

³emmanuel_obareki1@yahoo.com

ABSTRACT

In this research, Jigging, Froth Flotation and leaching have been used to beneficiate barite ore from Azara, Nasarawa State Nigeria. Chemical analysis on the ore indicates that it contains 53.09% of Ba and 11.52% S with a specific gravity value of 3.207 ± 0.03 . After the jigging operation, the specific gravity values of the underflow and overflow are 3.77 ± 0.029 and 2.77 ± 0.058 respectively while the Ba and S increased to 78.61% and 15.87% respectively. After the froth-flotation, the specific gravity values obtained are 3.95, 4.1 and 4.05 corresponding to pH values of 5, 7 and 9 respectively. Frothed barite with pH of 7 was leached with 0.2M HCl and a mixture of 0.2M HCl and HOCl. After leaching, the specific gravity values are 4.38 ± 0.03 and 4.27 ± 0.02 for HCl and HCl+HOCl respectively. The X-ray diffraction patterns show that highly crystalline peaks are obtained after froth flotation while more phases are added with leaching.

Keywords: Barite; Jigging; Froth Flotation; Leaching; Specific gravity

1. INTRODUCTION

Several industrial non-metallic minerals have been reported to be available in Nigeria but have either been left unexploited or have experienced very little exploitation [1]. One of such minerals is barite, a very important industrial raw material used as a pigment for making paints, in paper coating applications and more importantly as a weighting ingredient in drilling for crude oil. Due to its high specific gravity value, barite helps to counteract pressure formation during drilling thereby giving the drilling bit the necessary density required [2]. Other materials used as weighting agents include Celestite, Calcium carbonate, Ilmenite and synthetic Haematite. As the number of oil rigs around the world increases, the demand for barite will also continue to increase. Barite is usually the starting point in the manufacture of other compounds of barium.

The major export commodity for Nigeria is crude oil which is obtained from the hydrocarbon bearing regions of the country. A very important ingredient used in the drilling of crude oil is barite. Most of the barites currently used are imported because the ones being processed in Nigeria have specific gravity values which are lower than the industrially accepted standard. This is mainly due to the fact that a lot of impurities are associated with the barite ores. Azara

barite ore is one of many deposits that can be found in Nigeria. Through Petrology and Geochemical investigations, the mineralisation potentials of Azara barite deposits have been reported with relatively high amounts of BaSO₄ in the veins of the middle Benue Trough [3].

Several high quality barite samples have been reported in the literature to be beneficiated from low grade barite ores [4-7]. The strategies used to beneficiate these barite ores depend on factors like the grade of the ore, nature of the gangue and their liberation size [8]. Gravity separation which is about the oldest method to separate minerals and froth flotation are two of the most common methods used to beneficiate barite [9, 10].

Using froth flotation, barite samples with concentration of over 95% BaSO₄ have been obtained from different sources: tailings [4], from complex iron ore in Bulgaria [5] 96.32% and 91.26% respectively, from low grade barite ore from Myanmar [6] up to 88 % BaSO₄ from low grade barite in India [7]. Flotation of barite using *Eleasis guineensis*, analytical grade palmitic acid as collector and sodium silicate as depressant have led to recovery of up to 91.1 % BaSO₄ for Nigerian barite ore [11]. Modified starch has been used to remove fluorite from barite using froth flotation and the starch is

* Corresponding author, tel: +234 – 802 – 211 – 1311

believed to have acted as a depressant to barite in neutral solutions [12].

Computational processing through operations research has also been used to model and enhance the outcome of the jigging and flotation process [9]. The type of grinding mills used also determines the physical characteristics of barite like shape, roughness, wettability of the barite produced and there exists a correlation between the shape and wettability characteristics of the barite [13]. Grinding kinetics of calcite and barite minerals in terms of the specific rates of breakage, the primary breakage distribution function, also affect the shape of barite [14]. Leaching is also another beneficiation method for barite and has been used to process complex sulphide barite ore using Ferric chloride solution at temperatures between 80 to 150 °C [15]. Jigging, gravity separation and leaching has been used to beneficiate Azara barite ore with high specific gravity values obtained [16].

The objective of this research therefore is to formulate a beneficiation process that will lead to the production of a consistently high barite concentrate that is above 95% BaSO₄. The attainment of this objective will result in the reduction of the quantity of barite imported into the country. It will be of benefit to companies whose interests are in paint manufacturing, drilling, paper making etc. The country will also benefit since the amount of foreign exchange spent will be reduced while creating employment for a number of otherwise unemployed people.

A combination of jigging, froth flotation and leaching have been used to beneficiate Azara barite ore. Leaching was introduced because an initial study that was carried out indicated through the chemical analysis that after the froth flotation, the amount of silica still present in barite was still very high.

2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

The barite ore used for this investigation was collected from Azara in Nasarawa State, Nigeria. The barite ore 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. 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.

The process of separating barite from its ore commenced with the jigging operation, then froth flotation and finally leaching. Pine oil and oleic acid were used as the frother and collector respectively. The leaching was carried out at room temperature using hydrochloric acid (HCl) and hypochlorous acid (HOCl). 2000 g of the ore sample with particle sizes in the range - 180 to + 90 µm were used to produce the pulp of the ore for the jigging experiment. The pulp was fed into the jigging equipment with a constant supply of water. The overflow was collected into the collecting pan while the underflow was also collected and both were allowed to settle and dewatered. Both the underflow and the overflow were dried in an oven for about 5 h and their weights were measured.

300 g of the underflow which is the concentrate from the jigging operation was subjected to froth flotation by mixing with 2000 ml of distilled water. This was done in a Denver flotation cell operating at an impeller speed of 1500 rpm for about 5 mins to obtain proper suspension of solid particles within the pulp. Pine Oil, Oleic acid, HCl and NaOH are reagents that were used for the Froth Flotation process as frother, collector and pH regulators respectively. Four drops of the oleic acid were added to the pulp and conditioned for about 5 mins. Starch acting as a depressant was added and conditioning in vacuum was carried out for about 10 mins. The pine oil was added 2 mins before the expiration of the conditioning time while allowing air to be introduced at a reasonable rate. The froth was skimmed off the flotation cell into the collecting pan until barren froth persisted. The froth was allowed to settle, dewatered by filtration, washed and dried in the laboratory oven at 200 °C for 5 h. The depressed mineral was also dewatered, washed and dried. This procedure was repeated for pH values of 5, 7 and 9. 30 g of the concentrate from the froth flotation experiment was used for the leaching operation. The concentrate was poured into a conical flask mixed with 300 ml of 0.2M HCl. The mixture was gently washed and weighed. The product was filtered and dried in the oven. The same amount of concentrate in conical flask was also treated with a mixture of 0.2M HCl and HOCl in the ratio of 1:1 and then washed.

2.2 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:

$$\text{Specific Gravity} = \frac{\text{Weight of Mineral in Air}}{\text{Weight of Mineral in Air} - \text{Weight of Mineral in Water}} \quad (1)$$

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.

3. RESULTS AND DISCUSSION

3.1 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 indicated that apart from the major elements namely; barium and sulphur, about 18 other elements were observed. The sum of all these elements amount to about 15.14%. When the amounts of Ba and S are added together, they make up about 64.6% while Fe also has a very significant quantity contributing about 10.1%. This is similar to the composition in the literature concerning Azara barite [3]. The amounts of Ba in the barite after jigging, froth floatation and leaching with HCl increased to 78.6, 82.2 and 92% respectively. The amounts of the other elements decreased to 5.13%, 5.2% and <1% after jigging, froth flotation and leaching with 0.2M HCl respectively.

3.2 Specific Gravity

The specific gravity values of the barite before and after the beneficiation process is shown in Table 2. The measurement of specific gravity was carried out three times on each sample and then the obtained values were averaged. The barite head ore has a specific gravity value of 3.207 \pm 0.03. This value is low compared to the minimum industrially accepted value of 4.2. The reason for this can be traced to the high level of impurities observed from the chemical analysis.

3.3 Jigging Operation

Table 3 shows the result obtained from the jigging process. 50.0% of the feed was recovered as underflow (concentrates) while 47.0% of the feed was recovered as overflow (tailings) with the rest being the loss in material during the jigging operation.

Table 1: A table showing the chemical composition analysis of the barite before and after the beneficiation processes

Element (wt. %)	Al	Si	S	Cl	Ba	Mn	Fe	Sr	Au	Ta	Ni	Hf	Re	LOI	Cr	Co
As-received	0.9	1.41	11.5	0.1	53.1	1.77	10.1	0.38	0.02	0.03	0.28	0.06	0.06	20.7		
After Jigging	0.83	1.25	15.9	0.1	78.6	1.39	0.21	0.6	0.03	0.03	0.4	0.06	0.06		0.06	0.11
After Froth Flotation	0.59	1.39	12.5	0.1	82.2	1.62	0.2	0.6	0.02	0.03	0.4	0.06	0.07		LOD	0.12
After Leaching (HCl)			7.5	0	92											
After Leaching (HCl+HOCl)	0.83	1.25	12.9	0.1	67	1.39	2.2	0.6	0.06	3.32	0.4	0.06		8.56	1.23	0.11

Table 2: Specific gravity values of the Azara barite before and after the beneficiation processes

Sample Condition	S. G. Average	Standard Deviation	
As-received	3.207	0.0306	
After jigging	Underflow	3.77	
	Overflow	2.77	
After Froth Flotation	pH 5	Froth	3.95
		Depressed	3.22
	pH 7	Froth	4.1
		Depressed	3.12
pH 9	Froth	4.05	
	Depressed	3.15	
After Leaching	HCl	4.38	
	HCl + HOCl	4.27	

The chemical composition of the sample after jigging (Table 1) shows that although the concentration of the impurity elements decreases, they were not completely removed. There was a significant reduction in the content of iron from 10.1% to 0.21% after magnetic separation was carried out. The concentration of the impurities decreases to about 5.16% while that of Ba and S increases to 94.5%. The overall specific gravity (S.G) of the barite increases after this process. The S.G value for the underflow is 3.77 ± 0.029 while that of the overflow is 2.77 ± 0.0571 .

3.4 Froth Flotation

The result of the froth flotation process that was carried out on the Azara barite is shown in Table 4. 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 compared to the jigging process. The amount of sulphur slightly decreases to 12.5 % while that of barium increases to 82.2%. The concentration of barium in the froth at different pH values indicate that 81.8% was obtained at a pH of 5, 82.2% 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 3.95 ± 0.017 , 4.1 ± 0.026 and 4.05 ± 0.01 respectively.

3.5 X-ray Diffraction

Figure 1 shows the X-ray diffraction patterns for Azara barite ore and the sample with a pH of 7 after the beneficiation processes. A fitting of the barite ore with reference barite pattern in the ICDD database indicates

that it contains about 71.8% of BaSO₄. The analysis also revealed that in addition to the barite present, other minerals like SiO₂ and Fe₂O₃ 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 (96-900-4486) and found to contain about 86% barite. Annite which is a mineral with the chemical formula K_{1.84}Na_{0.14}Mg_{2.2} was also observed.

On leaching with acids, the crystallinity of the samples generally decreases with amorphous sections appearing on the diffraction patterns. A comparison between the pattern leached with 0.2M HCl and the reference in the database for barite (96-900-4486) indicates that the similarity index between them increases to more than 99%. Leaching with a mixture of 0.2M HCl+HOCl however led to a different outcome. Comparing the pattern with that of barite from the database showed that in addition to barite, other minerals like Hashemite, Anatase, and Magnetite were present. The similarity index was also lowered which is an indication that combining both acids is not a good idea.

However, leaching with 0.2M HCl and a combination of 0.2M (HCl and HOCl), transform to Hashemite which was not desired.

3.6 Leaching

When the samples were leached with 0.2M HCl, most of the impurities are believed to have dissolved leaving only trace elements of Cl, Zr, Nb and Mo. Leaching with a mixture of 0.2M HCl and HOCl acids, however did not help to remove the impurity elements from the barite as their amounts increases to 11.58% . It is possible that the reaction between the two acid mixtures instead of attacking the impurity elements, led to a reduction in the amount of barium from 82.2% to 67%. The S.G values further increased after the leaching process similar to the report by Nzeh and Hassan [16]. The value increased to 4.38 ± 0.025 with 0.2M HCl and 4.27 ± 0.015 with 0.2M HCl and HOCl.

Table 3: Result from the jigging Operation

Particle Size	Overflow		Underflow		Loss	
	Weight	%	Weight	%	Weight	%
- 180 + 90 μm	940g	47	1000g	50	60g	3

Table 4: Froth Flotation of barite carried out at different pH values

S/No	pH	Wt. of Froth (g)	Wt. of Depressed (g)	Loss
1	5	197.45	97.1	5.45
2.	7	201.72	94.65	3.63
3.	9	212.22	85	2.78

3.7 Scanning Electron Microscopy

The scanning electron microscope images of the leached samples are shown in figure 2. No significant change could be observed on the microstructures of both samples. Large and small grains with significant pores could be observed.

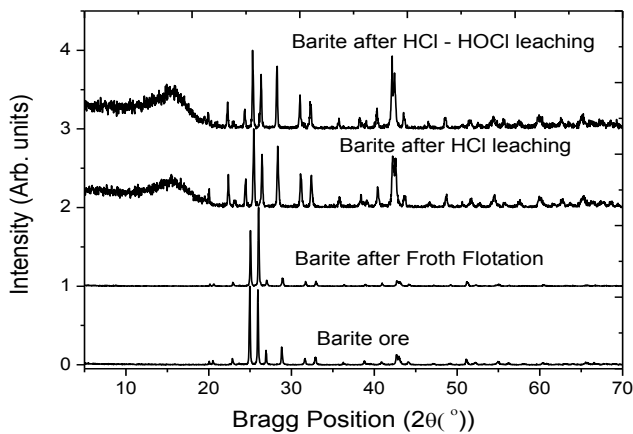
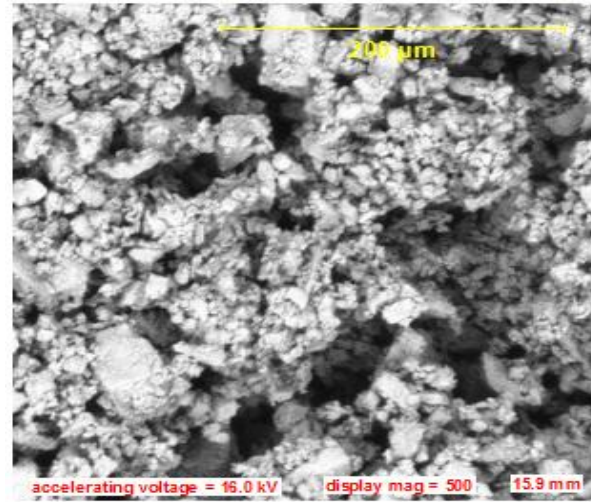


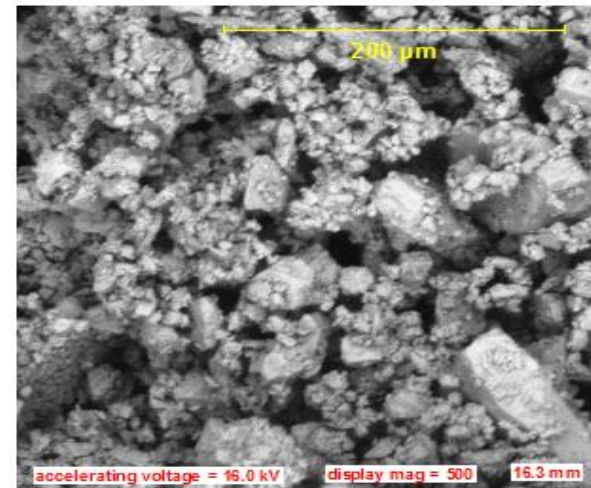
Figure 1: X-ray diffraction patterns for barite ore and processed barite with pH of 7

4. CONCLUSION

A combination of beneficiation processes namely Jigging, Froth Flotation and Leaching have been used to increase the concentration of both BaSO₄ 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 gave the highest specific gravity values. The X-ray diffraction data reveals that the diffraction pattern after leaching with a combination of HCl and HOCl is distorted while the chemical analysis indicates the formation of complex oxides. It is therefore not a good idea to leach with HOCl. The leaching with only HCl after using other beneficiation processes resulted in a specific gravity value of 4.38, crystalline diffraction peaks and chemical composition with as little impurity elements as possible. It can therefore be concluded that leaching with HCl is the way to go in the beneficiation of barite ores.



(a)



(b)

Figure 2: Scanning electron micrographs of barite samples that were subjected to: (a) jigging, froth flotation and leaching in 0.2 M HCl and (b) jigging, froth flotation and leaching in 0.2 M HCl and HOCl in 1:1 ratio.

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