CHARACTERISATION AND PROCESSING OF BARYTE ORES FOR OIL DRILLING APPLICATIONS

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DEDICATION

I dedicate this thesis to the glory and praise of the Almighty God, the most outstanding scientist of the universe, the giver of all wisdom, to my family, parents, and the overall benefits of humanity.

ABSTRACT

This study characterizes barite ores and uses environment-friendly and indigenous processes to develop technologies, methods and mineral processing tools for barite recovery from gangue minerals. The study is in four parts. The first project characterizes some Nigerian barite rocks and on-the-site processed barite as a weighting agent for oil drilling mud applications. In project II, the Nigerian barite rocks/ores were further processed by jigging. In the third and fourth projects, the impact of artisanal and small-scale barite mining and processing on human health and the environment was examined, assessed, and characterized to pursue sustainable development goals (SDGs) 3, 12, 13, and 14. The physicochemical and rheological properties of the on-the-site (locally) processed barite ores revealed that Nigeria barite could replace the industrially accepted barite used as a weighting agent for oil drilling mud. Barite ores were randomly selected, comminuted, screened, characterized, and beneficiated using a laboratory-built mineral jig. The effect of mineral liberation on separation efficiency, recovery, and yield was examined. The specific gravity of the barite ores was increased from 3.97 ± 0.0105 to 4.17 ± 0.20 and from 4.00 ± 0.0458 to 4.20 ± 0.2 without the use of chemicals. Likewise, higher barite recovery and yield were observed. Yet, the separation efficiency of the jigging process was low due to the presence of middling (a complex particle with gangue minerals associated with the value minerals). Project III also examined existing but weak institutional frameworks and policies for artisanal and small-scale barite mining. The results of safe mining assessment by ICP-MS and AAS analyses confirmed lead, barium, zinc, copper, and iron in the tailing effluents and barite pond. The survey showed that 54% of artisanal miners had health challenges traceable to illicit drugs and were ignorant about using safety kits during barite mining. The physicochemical studies for risk identification, assessment, and characterization revealed the extent of heavy metal contamination in mine water and tailing effluents for project IV. The toxicity and the extent to which the miners and entire mining community are exposed to the heavy metals contamination were evaluated, and the potential risks to human health due to barite mining and processing, estimated. The regular daily intake assessment and health quotient analysis revealed the accumulation of Pb and Ba is possible and can initiate chronic disease in humans over a long time. Some preventive measures to avert the carcinogenic risks of Ba and Pb were recommended to ensure a responsible and sustainable extraction of barite mineral mining.

KEYWORDS: Baryte ores, drilling fluid, mineral jig, artisanal barite mining, mining hazard, mine safety.

PREFACE

This work and the details provided in the dissertation is an original intellectual property of David Oluwasegun Afolayan. This was carried out at the African Development Bank (ADB) laboratory, African University of Science and Technology, Abuja, and the Geotechnical and Environmental laboratories, Worcester Polytechnic Institute, Worcester, Massachusetts, USA. The research work and discussions were done between May 2018 and December 2021 to fulfill the requirement for the award of Doctorate of Philosophy degree in the Department of Materials Science and Engineering at the African University of Science and Technology, Abuja, Nigeria. Also, it is noteworthy to mention that this research work was sponsored by the Regional Scholarship Innovation Fund (RSIF).

In truth, I was the lead investigator in this work and had the privilege of working with a team of experts, through whose support I could carry out all major research activities. This includes experimental design, device fabrication, data collection, curation and analysis, interpretation and discussion of results, manuscript composition, and publication of research findings. All these activities were examined and supervised by Professor Richard Kwasi Amankwah and Professor Carrick McAfee Eggleston. In addition to the supervisory authors, Dr. Mingjaing Tao, Dr. Adelana Rasak Adetunji, and Professor Peter Azikiwe Onwualu are part of the supervisory committee, involved in research concept formulation, methods and techniques verification, and manuscript composition.

This work presents the characterization, gravity concentration, and physicochemical study of artisanal mining and processing of baryte and its ores for a weighting material in oil drilling mud. Baryte ores are composed of several value minerals useful in different applications. These minerals include baryte and non-baryte minerals. Barytes are usually recovered from the ores with minor impurities such as water-soluble salts of calcium, potassium, magnesium, and sodium. Processing methods, techniques, and devices for optimum barite recovery were developed and fabricated. The locally processed baryte (on-the-site) were characterized, and the scientific explanation for their suitability in oil drilling mud was presented. The environmental impact of artisanal barite mining on miners and the mining community was assessed, potential health risks predicted, and recommendations were proffered to avoid negative consequences of unregulated barite mining and processing activities in Nigeria.

This work has seven chapters, three of which have been published in peer-reviewed journals (chapters 3, 5, and 6): Petroleum Exploration and Production Technology Journal, Mining Journal, and Sustainability Journal. Chapter 4 is under review by advisors.

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I am greatly indebted to my Ph.D. advisors, Professor Richard Kwasi Amankwah and Professor Carrick McAfee Eggleston. I sincerely appreciate the support of my Ph.D. supervisory committee members, Dr. Mingjiang Tao, Dr. Adelana Rasak Adetunji, and Professor Peter Azikiwe Onwualu. Also, a huge thanks to the acting Head of Department, Dr. Vitalis Anye, Managers, Mr. Russ Lang, and Dr. Wenwen Yao of the Geotechnical and Environmental Laboratories.

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PEER-REVIEW PUBLICATIONS

1. **Afolayan, D.O**., Adetunji, A.R., Onwualu, A.P. et al. Characterization of barite reserves in Nigeria for use as weighting agent in drilling fluid. J Petrol Explor Prod Technol 11, 2157–2178 (**2021, April**). https://doi.org/10.1007/s13202-021-01164-8

2. **Afolayan, D.O.**; Onwualu, A.P.; Eggleston, C.M.; Adetunji, A.R.; Tao, M.; Amankwah, R.K. Safe Mining Assessment of Artisanal Barite Mining Activities in Nigeria. *Mining* **2021 (September)**, *1*, 224-240. doi: 10.3390/mining1020015

3. **Afolayan, D.O.**; Eggleston, C.M.; Onwualu, A.P.; Adetunji, A.R.; Tao, M.; Amankwah, R.K. Physicochemical Studies for Risk Identification, Assessment, and Characterization of Artisanal Barite Mining in Nigeria. *Sustainability* **2021**, *13*, 12982. https://doi.org/10.3390/su132312982

LIST OF CONFERENCE PRESENTATIONS

1. Prospective of Microbes Assisted Beneficiation of Nigerian Barite: A Perspective by **Afolayan, D. O**., Ojeaga, I., Adetunji, A. R., Onwualu, A. P. presented at the 17th Annual International Conference of the Materials Science and Technology Society of Nigeria (MSN), RMRDC, Abuja, Nigeria (**November 2018**).

2. Safe Mining Strategies to Reduce Hazards Associated with Artisanal Mining in Nigeria by **Afolayan, D. O**., Adetunji, A. R., Onwualu, A. P. presented at the 9th International Conference of the African Materials Research Society (AMRS Botswana), held at the Gaborone International Conference Centre (GICC), Gaborone, Botswana (**December 2017**)

3. Beneficiation of a Nigerian baryte source for utilization as oil drilling mud by **Afolayan, D. O**., Adetunji, A. R., Onwualu, A. P. a poster presented at the 9th International Conference of the African Materials Research Society (AMRS Botswana), held at the Gaborone International Conference Centre (GICC), Gaborone, Botswana (**December 2017**)

1.0 CHAPTER ONE: INTRODUCTION

1.1 Background

Barite or Baryte is an unusually heavy non-metallic, insoluble in acids and water (its solubility is very low), with Mohr's hardness of 3-3.5, and its density of 4.48g/cm3. Unlike barite witherite (BaCO3), barite (barium sulphate) is chemically unstable. It does react slowly and can dissolve in water and cause environmental hazards (Salisu et al., 2015). The barite ore has a range of specific gravity between 3.5 and 5.3 (Afolayan, Adetunji, et al., 2021; Al-awad & Ai-qasabi, 2000; Brobst, 1958; Julphunthong & Joyklad, 2018). It contains between ~ 76-87% $BaSO_4$, gangue minerals of between 13% and 24% silica, iron oxide, quartz, celestine ($SrSO_4$), fluorite, chalcopyrite, and sulphide minerals such as galena (PbS), cinnabar (HgS), and greenockite (CdS) (Afolayan, Adetunji, et al., 2021; Chen et al., 2019; Ebunu et al., 2021; Raju et al., 2016; Wang et al., 2014). Nigerian barite contains very low mercury (Hg) and cadmium (Cd), making it very suitable for all types of drilling fluid applications (oil or water-based) (Afolayan, Adetunji, et al., 2021; Afolayan, Onwualu, et al., 2021; Brobst, 1958)**.** Nigeria is rich in barite and has over 21 million metric tons (MT) of barite – the fourth largest barite deposit in the world. Drilling grade barite is used in drilling for crude oil in Nigeria (Afolayan, Adetunji, et al., 2021; Al-awad & Ai-qasabi, 2000; OPEC, 2019). Similarly, Nigeria hosts 37 billion barrels of crude oil, which is ~ 2.2 % of the total world oil and the 10th largest crude oil reserve globally (Agbeyi et al., 2021; Faboya et al., 2016; Ighalo et al., 2020). It produces between 1.5 and 2.0 million barrels of crude oil per day between 2016 and 2020. However, Nigeria depends on imported barite for oil drilling applications. Over 80% of barite produced worldwide is used as a weighting agent in drilling fluids (Adeosun & Oluleye, 2017; Malden, 2017). World barite reserves are ~ 2 billion tons, but only 740 million metric tons have been explored and mined. China, India, Kazakhstan, Morocco, Thailand, the USA, Turkey, and other countries produced 9.5 million metric tons in 2018, worth 2.69 billion US Dollars (Afolayan, Adetunji, et al., 2021; Garside, 2020).

Crude or primary barite (run-of-mine) requires processing to meet minimum purity, density, and specific gravity standards (Afolayan, Adetunji, et al., 2021; Miller, 2013; Yakubu & Uthman, 2020). It is ground to a small, uniform size before it is used as a weighting agent for oil drilling mud specification for barite, filler, or extender, or addition to industrial products (Barlow & Kingston, 2001; Stark et al., 2014; Strachan, 2010). Weighting material with a specific gravity between 4.2 and 4.5 is used to increase the density of a liquid drilling fluid system. Barite ($BaSO_4$) is the most common weighting agent used today in all drilling fluids (Afolayan, Adetunji, et al., 2021; Al-awad & Ai-qasabi, 2000). The barite ore could occur at the mining sites as a vein, bedded, or residual deposits associated with gangue minerals. It is mined as either a solidified precipitate of hot barium-rich fluids in a fissure, dissolved surrounding or host rocks of bedded deposits, and barium enriched brines concentrated by a sedimentary basin. It is then ground to an American Petroleum Institute (API) specification (Afolayan, Adetunji, et al., 2021; Hanor, 2000; Van Kranendonk et al., 2008). Although barite is a by-product of mining lead, zinc, silver, or other metal ores, smaller mines utilize barite from veins formed by precipitation in hot subterranean waters (Dunham & Hanor, 1967; Hanor, 2000; Van Kranendonk et al., 2008). Due to increasing drilling activities, the demand for high-quality barite as a drilling fluid weighting agent has been increasingly challenging to meet. In addition, the supply of barite is geographically limited, with high transportation costs and substandard products. The consumption of drilling mud fluctuates from year to year, which is largely traceable to the price and amount of exploration drilling for oil and gas (Afolayan, Adetunji, et al., 2021; Afolayan, Onwualu, et al., 2021; Tanko et al., 2015). However, the demand for this essential mineral is relatively high. In Nigeria, the estimated market is up to 255,000 MT per annum and over 300,000 MT barite in 2020 (Afolayan, Adetunji, et al., 2021; Fayemi, 2016).

Barite ore, among others, contains non-barite minerals with associated metals such as Pb, Zn, Sn, Cu, Cd, Fe, and others (Gottesfeld et al., 2015, 2019). These elements and compounds constitute a threat to mining communities' health and well-being during mining and mineral processing (A. J. P. Adewumi & Laniyan, 2020; Afolayan, Onwualu, et al., 2021). Over 90% of barite mining activities in Nigeria are carried out by artisanal and small-scale miners (ASMs), and up to 75% of these miners operate informally, without mining licenses and rights. Such mining activities endanger human lives through the uncontrolled release of toxic heavy metals and other pollutants, which are major causes and consequences of severe health hazards in children and adults living close to the mining sites (A. J. Adewumi & Laniyan, 2021; Afolayan, Onwualu, et al., 2021; Laniyan & Adewumi, 2020). Amidst several possibilities and opportunities that abound in using barite for oil drilling mud application, barite must be extracted and processed in a responsible manner, obeying local and national mining laws (Afolayan, Onwualu, et al., 2021). This study assessed the suitability of some Nigerian barite rocks for oil drilling mud production. It designs processing methods and equipment that are reproducible and locally available to artisanal and small-scale barite miners and processors in Nigeria. The study also examined associated risks to the health of miners and mining communities and ensured responsible and sustainable barite mining aligned with the sustainable development goals (SDGs) 12, 14, and 15.

1.2 Problem Statement

Drilling-grade barite is specified by the API and must meet specific gravity (SG), chemical, and sizing requirements. Beyond specific gravity and density, physical and chemical requirements such as water-soluble earth metals present in barite ores, the particle size and shape must be consistent with the standards. Barite ores are mined in Nigeria by the use of explosives. This is done by stripping the overburden from the top of ore deposits. The he less dense top with the denser bottom material is blended (Oden, 2012). The era of the low-quality stigma associated with Nigerian barite from the trough has affected its marketability.

Barite rocks or ores usually contain barite and other undesired minerals which must be removed. These minerals are separated when barite is fully liberated, and each mineral grain is free. The use of chemical leaching, froth flotation, and hydrostatic pressure for barite recovery have been recommended and reported on a laboratory scale. However, these emerging barite processing methods are expensive, environment-unfriendly, and unsustainable. The cost of separating barite products from the chemicals, the surface modification of the minerals, and the consequence of heavy metal contamination of water and soil near the mining sites are currently significant issues of concern.

1.3 Unresolved Issues

The API standards for drilling grade barite specify more than specific gravity. There are other Physico-chemical standards, including criteria about size distribution, the quantity of calcium, extractable carbonate, moisture content, floatation chemicals, hematite, and other elements in the barite ore. Relevant research in this area has only focused on meeting the specification for SG and density without much emphasis on the purity, mineralogical, and chemical composition of the processed barite. Each gangue mineral has a selective extraction method and the level to which the API standards cover. Reducing the particle size of barite ore increases the degree of liberation and is critical to barite recovery.

The geological formation of barite results in different grades and is classified based on the volume of the gangue minerals intermixed during the solidification of the hot barium-rich fluid, brine, saline fluids concentrated by sedimentary fissures, or layers of barium-rich sediments. Usually, barite ores in larger particle sizes are washed and crushed into finer particle sizes. However, according to the company specification for barite, these should be screened into various grades based on their purity. In addition to these, many of the indigenous mining companies, Artisanal and Small scale miners (ASM) in Nigeria, have not adopted these practices, which have greatly affected the quality of the mined minerals. Moreover, the quality of barite differs with respect to the depth of the vein. Barite mineral at different depths is mined and processed together without screening. This adulterates the potentials of the mineral that possesses better qualities within and above the API specification and standards. The screening of products according to grades and qualities before barite milling is critical to other value-addition techniques and mineral processing. With this, the cost of crushing and beneficiation of barite should decline.

Surface mining has dominated the exploitation and exploration of most minerals in Nigeria. The assay and recovery of barite and other major gangue minerals are quite low. Most of these minerals have been lost or washed away within the wastewater. This has resulted in the dispersion of the minerals, increases in soil toxicity, and other environmental degradation. Hence, the recovered concentrate does not consolidate the actual volume of the run-of-mine. Due to this dilemma, research results and data from several experimental works on barite do not correlate and reflect the geological evidence. Nigeria's barite research and development have remained ineffective due to the weak local involvement and industrial participation. The Government-researcher-industry-community nexus needs to be formulated and fully established before formalizing the activities of artisanal and small-scale barite miners in Nigeria.

Barite mineral, although non-carcinogenic, may be associated with lead sulfide (PbS) and encrusted with FeS_2 or Fe-FeS_2 microcrystals. Sulfuric acid mine runoff is unavoidable when barite tailings containing sulfide minerals are exposed to water and oxygen (A. J. Adewumi & Laniyan, 2021; A. J. P. Adewumi & Laniyan, 2020). Thus, it is necessary to assess the poisonous level of barium, lead in galena, cadmium, copper, and other toxic elements in barite ore. These heavy metals form part of the total toxic index of the environment. Thus, it is necessary to examine the total toxic levels of the contaminants and assess the safety of miners, mining communities, mammals, and the entire ecosystem. The knowledge generated will help modify ASMs in Nigeria.

1.4 Objectives

The aim of this study was to develop technologies and methods for processing Nigerian barite rocks for oil drilling mud application using environment-friendly methods and indigenous processing devise to attain the sustainable development goals (SDGs) 3, 12, 13 & 14.

The objectives include to:

i. Characterize some Nigerian barite rocks and on-the-site processed barite for oil drilling mud application;

ii. Design and fabricate laboratory/home-built/indigenous mineral jig for barite processing/beneficiation;

iii. Determine the effects of mineral liberation on barite separation and recovery by jigging

iv. Identify, assess, and characterize sources of hazards at artisanal barite mines and risks to the health of miners and mining communities.

1.5 Scope of Work

This research work encompasses the following sub-objectives or activities:

- Mining sites visit and sampling of some barite rocks and mine water
- Characterization and physicochemical analysis of barite rocks
- Crushing and grinding (comminution) of barite rocks

- Mud formulation and fluid characterization for rheological properties to evaluate the effect of barite addition into the formulated drilling mud
- Screening of pulverized barite rock (sizing into -75 µm, -106 µm, -150 µm, and -250 µm)
- Design and fabrication of laboratory-built mineral jig
- Processing and recovery of barite from undesired minerals to increase specific gravity (SG)
- Characterization of jigging products (overflow/tailings and underflow/concentrate)
- Digestion of pulverized barite rocks and characterization of mines water and tailings' effluents
- Physicochemical studies and heavy metal contamination assessment of barite ponds and tailings' effluents
- The characterization and analysis of identified mining risks and their consequences on the health of miners, residents, and the mining community.

1.6 Dissertation Layout

This dissertation is in seven chapters.

Chapter 1 encompasses the general introduction and overview of the dissertation, presenting general and specific background, research problem, unresolved issues, the scope of work, and dissertation layout.

Chapter 2 uncovers previous works on the characterization of barite for oil drilling mud application and the beneficiation of barite ores by gravity concentration, chemical leaching, and froth flotation. The activities of artisanal and small-scale miners, statements of the mining act, and policies were reviewed for the formalization/regulation of artisanal and small-scale mining of barite ores. Different processing methods and capacities of mineral processing equipment were described. The section was concluded with the heavy metal contamination of water by mine water and tailings' effluents due to unregulated barite mining and mineral processing.

Chapter 3 presents the results of investigations of local mining and mineral processing methods, explains the physical, chemical, and rheological properties of locally (on-the-site) processed barite ore. The section also examines the suitability of the processed barite as a weighting agent and studies the effect of adding locally-processed barite in formulated API drilling mud.

Chapter 4 explores a parallel quality contrast of barite ores across particle size ranges, determines the optimum jigging conditions (jig frequency, water velocity, and jigging time), and feed characteristics for efficient barite recovery. It also studies the contribution of particle size and particle density (degree of liberation) on barite segregation and separation from other undesired minerals within the barite ore.

In chapter 5, sources of heavy metal contamination in abandoned and active barite ponds were identified. The consequences of heavy metal consumption by miners on human health and the environment were assessed using data from questionnaires and water analysis.

Chapter 6 presents the physicochemical studies of heavy metal contamination. The associated risks and exposure levels of miners and the mining community and their consequences on health and wellbeing were assessed. Risk levels were characterized and analyzed using primary and secondary data (environmental standards).

Chapter 7 contributes to the body of knowledge, presents vital concluding remarks from this study and recommendations for future work.

1.7 Publications

The content of the dissertation has been published in Journals indexed in SCOPUS, Web of Science and Google Scholar. The publications are:

4. **Afolayan, D.O**., Adetunji, A.R., Onwualu, A.P. et al. Characterization of barite reserves in Nigeria for use as weighting agent in drilling fluid. J Petrol Explor Prod Technol 11, 2157–2178 (**2021, April**). https://doi.org/10.1007/s13202-021-01164-8

5. **Afolayan, D.O.**; Onwualu, A.P.; Eggleston, C.M.; Adetunji, A.R.; Tao, M.; Amankwah, R.K. Safe Mining Assessment of Artisanal Barite Mining Activities in Nigeria. Mining **2021 (September)**, 1, 224-240. doi: 10.3390/mining1020015

6. **Afolayan, D.O.**; Eggleston, C.M.; Onwualu, A.P.; Adetunji, A.R.; Tao, M.; Amankwah, R.K. Physicochemical Studies for Risk Identification, Assessment, and Characterization of Artisanal Barite Mining in Nigeria. *Sustainability* *2021*, *13*, 12982. *https://doi.org/10.3390/su132312982*

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2.0 CHAPTER TWO: LITERATURE REVIEW

2.1. General Introduction

This chapter introduces barite as a heavy non-metallic mineral that possesses useful qualities for drilling and other industrial applications. The occurrence or mineralization of barite and its association with other minerals within the host rocks are discussed. The characteristics and quality contrasts of barite ores across veins or deposits are reviewed about exploration and pre-mining processes. Artisanal barite mining and barite characterization are also discussed. The basis of barite processing, types, and locations of barite deposits, different uses of barite, material, and slurry handling to ensure proper disposal of tailing effluents and avoid heavy metal contamination are discussed in detail.

2.2 Barite Ore

Baryte is the most common mineral of barium with the chemical formula $BaSO_4$ in the proportion of 66% BaO and 34% SO_3 (pure barite) (Bonel, 2005)**.** It is naturally-occurring barium sulphate ($BaSO_4$) used most predominantly for industrial purposes. It owes this industrial value to its density or weight and has a specific gravity of 4.5. The mineral may occur in veins, stratiform beds, and lenses in addition to residual deposits. The largest deposits currently mined are stratiform beds in China, India, and the US. In Nigeria, the three major geological types of barite ore deposits occur in vein, cavity filling, and residual or bedded deposits. Barite seldom exists in nature as a pure end member but rather as a solid solution. This may appear to be continuous between the baryte and celestine ($SrSO_4$) but then discontinuous with anhydrite ($CaSO_4$) (Bonel, 2005; Dunham & Hanor, 1967; Hanor, 2000; Monnin & Cividini, 2006; Zhu, 2004). Ba in barite ($BaSO_4$) may be substituted by other cations (K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ra^{2+}, Pb^{2+}, La^{3+}, Ce^{3+}, Lu^{3+}, Eu^{2+}) and give rise to the following minerals as associated minerals within the ore. This includes: celestine ($SrSO_4$), galena (PbS), sphalerite (ZnS), pyrite (FeS_2), quartz (SiO_2), calcite ($CaCO_3$), dolomite ($Ca,Mg(CO_3)$), marcasite (FeS_2), chalcopyrite ($CuFeS_2$), fluorite (CaF_2), siderite ($FeCO_3$) and witherite ($BaCO_3$) (N A Labe et al., 2018; Ngukposu A Labe et al., 2018a; Nwoko & Onyemaobi, 1997; Oladapo & Adeoye-Oladapo, 2011). The distribution of major barite deposits in some parts of Nigeria is presented in Figure 2.1.

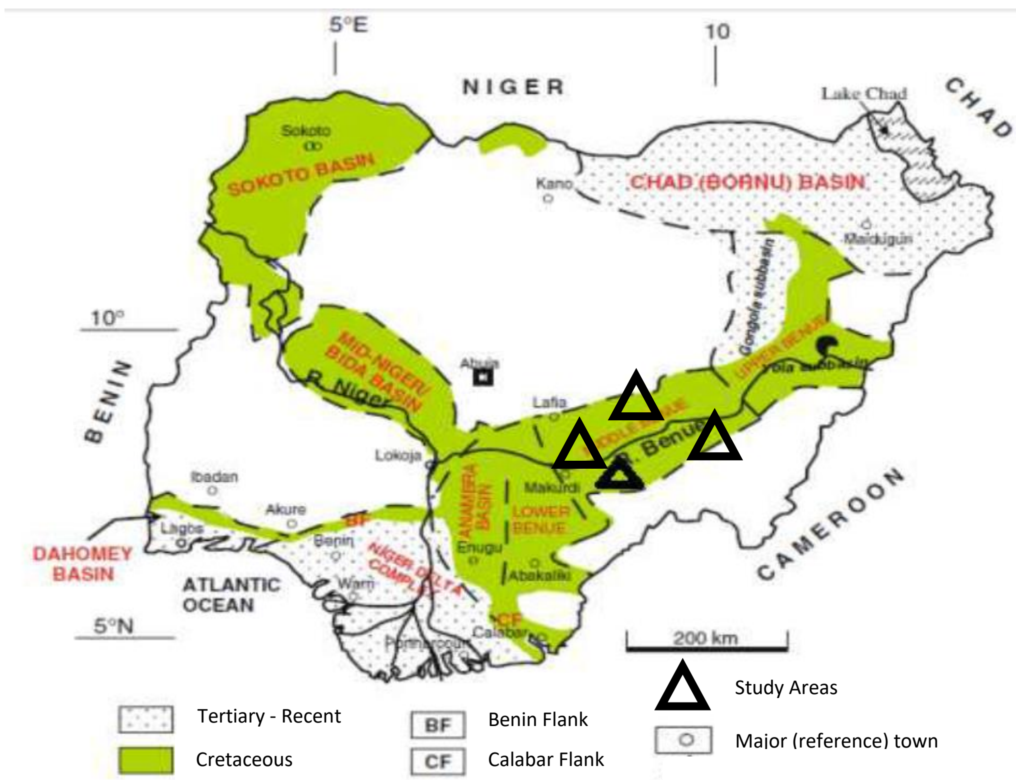

Figure 2.1: Map of Nigeria showing the Barite mineralized Zones around the Benue Trough (modified from (Ehirim et al., 2016))

Barite deposits in Guma (Benue State), Ibi (Taraba State), and Wase (Plateau State) hold a lot of promise, even though its known veins are currently fewer than in the Azara field in Nasarawa State (David Oluwasegun Afolayan, Adetunji, et al., 2021; Oden, 2012). An equatorial climate characterizes the barite mining sites with dry and wet seasons and an average daily temperature between 25°C and 35°C across the year (Ankidawa et al., 2020; Gabriel et al., 2020). The wet season usually covers April to October, with the mean annual rainfall between 1000 mm and 1350 mm. Moreover, with the Benue and Taraba Rivers as the major basin, the area is heavily subjected to gullies and massive flooding due to natural events (hazards) and anthropogenic activities (barite mining). There are ferruginous tropical and alluvial soils (classified as Ferric Luvisol and Fluvisols) derived from the basement complex's crystalline acid rocks, within the Trough. Wase site is characterized by quaternary sedimentary deposits, weathered and tectonically fractured zones of crystalline rocks. Groundwater circulation occurs partly through fractured crystalline and volcanic rocks and within alluvial, eluvial, colluvial, and chemically degraded deposits. These aquifers host and distribute soil water and are disturbed by mining activities. In the case of flooding, water from abandoned and active barite mines contaminates the rivers (Gabriel et al., 2020).

The concentration of barium and sulphate ions in the hydrothermal fluid results in barite quality contrast between the top part and the lower portions of the vein. Higher quality barite tends to come from the lower portions, which increases with depth. The quality of the Nigerian barytes is moderate to high, with fewer cases below the minimum global specification (Fatoye et al., 2014; Oden, 2012). This disparity is due to major impurities such as quartz, iron oxide (goethite), fluorite, and carbonates of iron, calcium, and magnesium (David Oluwasegun Afolayan, Adetunji, et al., 2021). These impurities reduce the specific gravity and increase the hardness of the unprocessed barytes, the processing cost, and the mills' wear rate. The goethite and silica impurities can be removed by magnetic and gravity separation. Once processed, the specific gravity of the Nigerian barytes increases and meets 4.20 specified values by American Petroleum Institute (API) (Fatoye et al., 2014; Komadja et al., 2021; Oden, 2012).

Barite is used as a weighting material in drilling mud to prevent blowouts by sustaining the borehole pressure (David Oluwasegun Afolayan, Adetunji, et al., 2021; Sadiq et al., 2003; Strachan, 2010). This is obtained by mixing barite in water with other materials (drilling mud additives) to form mud and is pumped into the drill hole. The bottom-hole pressure created by the drilling fluid should equal or exceed the pressure in the surrounding formation to prevent blow-outs and to prevent formation collapse during drilling. Primary barite used as a weighting agent includes crude barite and processed products of simple beneficiation methods, such as washing, jigging, heavy media separation, tabling, flotation, and magnetic separation. This mainly requires grinding to a small, uniform size before applying as a weighting agent in petroleum well drilling mud (API or OCMA specification barite). Barite used for drilling can be blue, black, brown, or gray, depending on the associated gangue minerals. However, such barite is also expected to be dense, soft, and chemically inert. In addition to these, the American Petroleum Institute (API) specifications recommended specific gravity of 4.2 or more, an allowable percentage of iron oxide, free-soluble salts, and that 90% to 95% of the material must pass through a 325-mesh screen (David Oluwasegun Afolayan, Adetunji, et al., 2021; Al-awad & Ai-qasabi, 2000; Sadiq et al., 2003; Strachan, 2010).

2.3 Field Characteristics and Quality Issues of across Vein, Residual and Bedded Deposits of Barite Mineral

Barytes occur in various geological environments and exist in sedimentary rocks, which act as host rocks. The introduction of hydrothermal fluids into the ocean provides necessary conditions that favours baryte precipitation. Several works are reported on barite deposits and mineralization around the Benue Trough. However, the vast deposits and high-quality minerals within areas of study remain one of the positive aspects of the Trough (David Oluwasegun Afolayan, Adetunji, et al., 2021; Akpeke et al., 2006; Ekwueme et al., 2015; Ekwueme & Akpeke, 2012; Fatoye et al., 2014; N A Labe et al., 2018; Ngukposu A Labe et al., 2018a; Oden, 2012). Presently, the Trough is rich in baryte and galena, and other minerals are yet to be discovered (Akpeke et al., 2006; Ekwueme & Akpeke, 2012; Oden, 2012). Some rocks hosted barytes within the Trough. This includes sandstones, mudstones of the Cretaceous period, ironstones, siltstones, and shale. The quality of barite and other associated minerals explored from the Trough attracts the attention of the Minister of Solid Minerals, Ministry of Mines and Steel Development (MMSD) and the oil industry (D.O. Afolayan, 2017). However, the quality of the ores vary across depth and from one position to another. It also vary from one mining site to another. Research has shown that two types of baryte occurrences exist within the Trough. The sediment-hosted or concordant type has an hydrothermal origin and frequently multilayered (Ngukposu A Labe et al., 2018a; Oden, 2012). It is less frequent and can be seen in the Ibi baryte field (one location under the present study). Similarly, vein occurrence is the most common baryte deposit and is usually sandwiched by quartz and other gangue minerals. This type of deposit is huge and a single pit has a reserve estimate of over 200 000 tons/m^3 of barite deposits (D.O. Afolayan, 2017; David Oluwasegun Afolayan, Adetunji, et al., 2021; PIN, 2017). Figure 2.2 shows mined barite pits for barite veins and deposits within the study areas, an example of the vein type barite occurrence within the Trough.

(a) (b)

Figure 2.2: baryte mine pits showing a typical example of the vein type (a) and stratiform type (b) barite occurrence in the middle Benue Trough.

Barite samples analyzed in this study are mined from the pits (D.O. Afolayan, 2017). These pits are uncovered and water from the “barite ponds” can contaminate other water resources used for drinking and other domestic activities

2.4 Distinguishing Characteristics and Types of Baryte

2.4.1 Distinguishing Characteristics of Baryte

The high specific gravity of baryte is its main useful feature. It is relatively insoluble in acid and water (its solubility is very low) and distinguished from anhydrite and celestine by its orange fluorescence and green flame in a flame test. Its crystal shape has two perfect cleavages [{010} and {210}] and one imperfect cleavage [{010}], and lack of fluorite fluorescence differentiate it from fluorite (Patel & Koshy, 1968). As an ionic solid, this barium sulphate is composed of Ba^{2+} ions and SO_4^{2-} ions. Its component oxides are BaO: 65.7%, and sulphur trioxide (SO_3): 34.3%.

The chemical formula for barite is $BaSO_4$, and its basic property varies and ranges with major compositional impurities. Baryte is a transparent crystalline material with the colour varying from colourless to white and light shades of yellow, blue, brown, and grey depending on the type and colour of the gangue minerals (impurities). It has a molecular weight of 233.4 grams per mole, a density of 4.48g/cm^3, and is relatively insoluble in water (dissolve or react very slowly). Table 2.1 shows the thermodynamic solubility of different sulphate minerals. The table presents baryte as one of the minerals with the least thermodynamic solubility (Krumgalz, 2018). It has an orthorhombic crystal system, a tabular parallel to the base, fibrous, modular to massive. It has an irregular and uneven fracture (flat surfaces fractured in a variable pattern) (A & Staudhammer K, 1967). Its hardness ranges between 3 and 3.35 on the Mohs scale (David Oluwasegun Afolayan, Adetunji, et al., 2021; Ekwueme et al., 2015; Ekwueme & Akpeke, 2012; N A Labe et al., 2018; Ngukposu A Labe et al., 2018a; Omoniyi & Mubarak, 2014).

Table 2.1: Thermodynamic solubility of some minerals sulphates [26,29]

Sulphate Minerals	K_{sp}
Baryte ($BaSO_4$)	$0.89 \times 10^{-10} - 1.995 \times 10^{-10}$
Celestite ($SrSO_4$)	$2.173 \times 10^{-7} - 4.038 \times 10^{-7}$
Gypsum ($CaSO_4$. $2H_2O$)	$2.3 \times 10^{-5} - 4.821 \times 10^{-5}$
Hemihydrate ($CaSO_4$. $0.5H_2O$)	$1.34 \times 10^{-4} - 1.845 \times 10^{-4}$
Anhydrite ($CaSO_4$)	$1.995 \times 10^{-5} - 7.079 \times 10^{-5}$
Meridianiite ($MgSO_4$. $11H_2O$)	$1.18 \times 10^{-2} - 4.1 \times 10^{-2}$
Epsomite ($MgSO_4$.$7H_2O$)	$1.3 \times 10^{-2} - 3.48 \times 10^{-2}$
Arcanite (K_2SO_4)	$1.52 \times 10^{-2} - 1.71 \times 10^{-2}$
$Na_2SO_4.7H_2O$	$1.89 \times 10^{-1} - 2.04 \times 10^{-1}$
Thenardite ($NaSO_4$)	$4.94 \times 10^{-10} - 5.56 \times 10^{-10}$

Barite solubility is 1.8×10^{-5} mol/kg H_2O at 75°C - 100 °C

2.4.2 Types of Baryte Deposits

Baryte deposits are found in a variety of geological environments. The three major types of barite deposits are stratiform, vein, and residual. The earliest mining activities were from veins, often associated with lead, zinc, and residual deposits. Most baryte in Nigeria and around the world is produced from stratiform deposits (Oden, 2012).

2.4.2.1 Stratiform Deposits

These are formed by the barite precipitation at or near the seafloor of sedimentary basins or exhalative (sedimentary exhalative [sedex]) deposits. The brines are generated by the migration of reduced saline fluids concentrated by major basin-controlling faults. They are often associated with base metal sulphide and occur in rocks varying in age from Precambrian to Cenozoic. These deposits are less frequent and seen in Alifokpa in Cross River State, Gidanwaya, and Gidan Waya in Taraba State. Stratiform barite deposits of Mangampet in Andhra Pradesh, India, have two stratiform lenses up to 1.2km long and 20m wide. It has enormous deposits of over 74 million tons of barite with an annual production of 700,000 tons. It contributes about 90% of the baryte production in Andhra Pradesh (Bonel, 2005).

Similarly, in Cambrian black shales, the Jiangnan region of south China and the Quilling region in the Yangtze valley have sedex deposits with almost 4 million tonnes per year. It contains some witherite and baritocalcite ($BaCa(CO_3)_2$) deposits associated with the barite horizons. The deposit in the Nevada barite belt, western USA, extends over 500km from north to south and is about 125km wide. Its estimated reserve is around 90 million tonnes of barite in hundreds of tiny lenses in siliceous sediments. Other significant stratiform deposits occur in late Proterozoic meta-sedimentary rocks near Aberfeldy in Scotland, the Primorye region of far-eastern Russia, Devonian shales in Germany, and Mesozoic carbonates in a belt from Pakistan through Iran (Bonel, 2005; N A Labe et al., 2018; Ngukposu A Labe et al., 2018b; Oden, 2012).

2.4.2.2 Vein and Replacement Deposits

These are classified into small and sizeable vein-style barite deposits. They were exploited before the 1980s until large sedex deposits became more critical. Due to fluid mixing or reduced pressure and temperature, these deposits are formed by the precipitation from hot barium-enriched fluids in faults and fractures. However, the liquids may dissolve the surrounding rocks (mainly limestone and dolomite) to form irregular replacement deposits. Several veins and replacement deposits exist in Nigeria (Bonel, 2005; MMSD, 2010). The most impressive barite veins are in the Azara area, Ribi, Keana, Aloshi, Ambua, Chita, Kuduku, Wuse, and Akiri in Nasarawa State; Torkula, Kaseyo, Zanzan, Makurdi, Lessel area (Lessel Bunde, Lessel Mbato and Lessel Mbagwa), Gboko, Yandev and Ihugh barite fields in Benue State, Nigeria; Didango, Ibi, and Kumar barite in Taraba State, Nigeria. It also exists in Yala and Gombe barite fields, Nigeria (N A Labe et al., 2018; MMSD, 2010; Oden, 2012). Vein deposits exist in Britain, Morocco, USA, Germany, and Slovakia. The Ballynoe vein deposits in Ireland have over 5 million tonnes of direct shipping baryte production capacity and occurred as a single lens associated with replacement Pb-Zn mineralization in lower Carboniferous carbonate. The veins consist predominantly of barytes (80% $BaSO_4$ and less than 5% $SrSO_4$), sulphides (galena, pyrrhotite [FeS_2 – magnetic pyrite]), iron, manganese oxides, as well as fluorite, calcite, and quartz. These deposits are generally smaller than the bedded deposits, including Dreislar and Rhineland-Palatinate vein deposits in Germany, Les Arcs deposit in France, and Pennine ore fields in the United Kingdom (Bonel, 2005; Fatoye et al., 2014; Lorenz & Gwosdz, n.d.).

2.4.2.3 Residual or Bedded Deposits

These barite deposits are formed by the dissolution of the host rock of bedded deposits, leaving irregular masses of barite in a clay matrix. Such deposits are incredibly variable in size and shape but can extend over several kilometers. Individual beds are fine-grained, huge to laminate, and contain about 50 – 95% barite. They are the most valuable and economically crucial deposit type because they are usually large and have higher grades (Brobst, 1958). Clark et al. (1990) further subdivided the bedded baryte deposits into five groups based on their depositional environment and the presence of base-metal sulphides. Torkula barite field in Hungwa, Nigeria, is characterized by bedded barite deposits. It comprises several veins stacked together to form a bed (N A Labe et al., 2018; Ngukposu A Labe et al., 2018a; Oden, 2012; PIN, 2017).

2.5 Exploration and Exploitation of Barite Minerals

The exploitation of mineral resources has anticipated leading significance in several developing countries, including Nigeria. Most importantly, Nigeria has abundant mineral resources, contributing immensely to the national wealth with associated socio-economic benefits. Mineral resources amidst other reserves have to pass through the exploration, mining, and processing stages before they are harnessed (Adekoya, 2003; Ajakaiye, 1985). However, different types of environmental damage and hazards inevitably accompany the three stages of mineral development (David Oluwasegun Afolayan, Onwualu, et al., 2021). Relatively more recently in the oil and gas industries, barite, limestone, marble, and rock aggregates have been increasing in national socio-economic development and growth (Aigbedion & Iyayi, 2007). As the wealth from hydrocarbons and crude oil reserves continues to diminish with the growing uncertainty in global demand and supply, all attention is being fixated on solid minerals as alternative sources of revenue and employment for the teeming population. Similarly, most solid mineral occurrences in Nigeria are located in the Benue trough (David Oluwasegun Afolayan, Onwualu, et al., 2021; Aigbedion & Iyayi, 2007; N A Labe et al., 2018; Ngukposu A Labe et al., 2018a; Oden, 2012; Omoniyi & Mubarak, 2014; PIN, 2017; *Mineral Deposits in Nigeria*, 1959).

The exploration of near-surface mineral deposits has become increasingly difficult due to the complexities in geology. However, several geophysical techniques have been adopted in search of barite ore deposits (Bishop & Emerson, 1999; Meju, 2002). Each of these techniques depends upon detecting variations in one or more of the physical properties of rocks such as Electrical resistivity, Density, Magnetic susceptibility, and Seismic velocities, which vary within wide limits. Baryte has a high resistivity compared to its host rock. This makes it easily detectable by the electrical method because of the resistivity contrast with the host rock. Electrical resistivity methods have variously been used to explore baryte veins by several researchers. These studies revealed that high resistivity signatures are associated with barite vein structures (Arinze & Emedo, 2021; Ehirim et al., 2016; G. E. Ene et al., 2019).

2.6 Quality of Barite Deposits in Nigeria: An Extensive Outlook

In Nigeria, the baryte grains at the center of the barite vein are considered pure grade, while barite at contact with the wall rock is a moderate grade (Ayim & Enoch, 2009). This classification is based on the quality of material and industrial applications. The high-grade varieties can be used in oil and gas industries while the low-grade is used in the paint and glass industries. Usually, the grade 1 barite contains the smoky and whitish varieties and has a minimum of 92% $BaSO_4$, while grade 2 is described as pinkish varieties with 77% $BaSO_4$. However, both grades cannot be used in their raw form until processed (Ayim & Enoch, 2009; E. G. Ene et al., 2012). Typical barite veins in Nigeria appear to originate in the basement complex beneath the Cretaceous sedimentary cover. This makes the mineralization more epigenetic.

The vein orientations are strongly and structurally controlled based on their formation and parallel to the prevailing maximum compressive stress. Similarly, such directions enable grain growth and vein expansion parallel to the low energy orientation (E. G. Ene et al., 2012; G. E. Ene & Okogbue, 2016; Oden, 2012). The extent to which a vein expands depends on the concentration of barium sulphate in the hydrothermal fluid, the fluid volume and pressure within the geological environment. Narrow barite vein emerges when barite precipitates from an hydrothermal fluid are depleted of barium and sulphate ions or sandwiched with a high volume of gangue minerals (e.g., microcrystalline quartz) at low pressure. Such makes up ~ 95% of barite occurrences within the Trough. Several promising fields have been identified for the large-scale monetization of baryte mining in Nigeria (E. G. Ene et al., 2012; G. E. Ene & Okogbue, 2016; Oden, 2012). Beyond these fields, there are more other veins producing medium to high-quality barite than those of low-quality material, as clearly shown in Table 2.2

Table 2.2: Quality Variation of Barite deposits in Nigeria (D.O. Afolayan, 2017; Oden, 2012)

Low Quality (SG: 3.0-4.0)	Medium Quality (SG: 4.0-4.2)	High Quality (SG: Above 4.2)
Aloshi, Azara, Wuse,	Ribi, Afuze, Ambua	Ibi, Afuze, Alifokpa
Pupule, Mubi, Apawa,	Ntak, Yandev, Pila-Tandev	Makurdi, Bundin-Kwaj-ali
Tombu, Bunde Lessel,	Lessel, Obubra, Kornya	Igara, Yala, Afugo, Guma
Port Harcourt, Lessel	Kumar, Ihugh, Azara,	Gabu, Osina, Konshisha
Kuduku, Obubra, Keana,	Guma, Orgba, Mayo-Belwa	Didango, Kumar, Torkula

2.6.1 Barite in Taraba State, Nigeria

Taraba State in Nigeria constitutes a significant part of the Middle Benue Trough and hosts barite in five of its LGAs: Ibi, Lao, Yoro, Sardauna, and Karim Lamido. This barytes resource is compared in the igneous-metamorphic rocks of the Pre-Cambrian, also in sandstone, shale, mudstone, siltstone, and limestone of the Benue Trough Sedimentary Formations (Fatoye et al., 2014; Omisore et al., 2016). However, its mineralization and deposition are fissures filling with hydrothermal solutions formed by the closing in of the Benue Trough. The resource is hosted in porphyritic granites and fine-grained sandstones at these mineralized zones and locations. Similarly, vein length persists and extends over 3.5 to 5km range, and its width ranges from 3.5 to 5 meters. Although high-grade barite ore is used for industrial applications, it usually contains quartz, galena, and sphalerite. These impurities are adequately separated to enrich the barite mineral (D.O. Afolayan, 2017; MMSD, 2010; Nnaemeka, 2014). The inferred barite resource base in Taraba State, Nigeria, is approximately 8,960,000 metric tons, measured to 20m depth or more. Most significantly, the deposit quality is appropriate for the API Specifications, with most of the resources having specific gravity close to 4.2 (MMSD, 2010).

2.6.2 Baryte in Plateau State, Nigeria

The barites deposits in Azara and Wase occur as hydrothermal veins within the Cretaceous Keana sandstone of the Middle Benue Trough. This best-known deposit of barites in Nigeria has about twenty identified hydrothermal veins. These mineralized veins were found to contain Calcite, Fluorite, and Celestine ($SrSO_4$) as gangue minerals, generally striking in the NE-SW, NW-SE, and E-W directions (Chaanda et al., 2010). However, the presence of these impurities has lowered the overall specific gravity. There are good quality barites in Faya, Plateau State. A prominent well-developed vein was estimated to contain about 500,000 metric tons of resource, with the overall specific gravity (with impurities) varying between 4.0 and 4.2. These deposits contain very low mercury (Hg) and cadmium (Cd), making them environmentally safer and also suitable for drilling offshore (Fatoye et al., 2014; MMSD, 2010).

2.6.3 Baryte in Benue State, Nigeria

Baryte mineralization in the Middle Benue Trough occurs in Gboko, Guma, Torkula, Hungwa, Gwer, Ushongo, Markudi, Konshisha. In Benue State, baryte deposits are contained in the Pre-Cambrian igneous-metamorphic rocks and the Benue trough sedimentary formations consisting of sandstone, mudstone, siltstone, limestone, and shale. These baryte deposits occur in hydrothermal solutions filling fissures and are formed by the interaction of infiltrating solutions containing barium with soluble sulphates aided by major tectonic activities in the Lower Benue

Trough during the Santonian (MMSD, 2010; Ola Peter Sunday et al., 2020). The barite mineral may occur as white, reddish-brown, and clear varieties, with specific gravity (SG) varying between 3.7 and 4.4 (A.I. Ebunu et al., 2021; Fatoye et al., 2014; Nnaemeka, 2014).

Geochemical analysis carried out by the Ministry of Mines and Steel Development (MMSD), Nigerian Geological Survey Agency (NGSA), and Nigerian Metallurgical Survey Agency (NMSA) revealed that most baryte samples from various locations contain between 76 and 87% $BaSO_4$, 5, and 21% Silica (SiO_2) and up to 3% iron oxide (Fe_2O_3). Similarly, baryte veins in these locations are usually 3m wide and 20m deep or more. Nevertheless, when exposed, they do not persist over long distances. The vast market, quality materials with an average Specific Gravity of 4.0, and the estimated reserve base of 307,657 metric tons make baryte mining and processing a viable investment (A.I. Ebunu et al., 2021; MMSD, 2010).

The quality of Nigerian barite deposits and their constituent impurities vary from one place to another. The concentrations of $BaSO_4$ in hydrothermal fluids in the trough were conceivably low during the Cretaceous period. In most barite veins, the quality of deposits at the top of the formation differs from the lower portions. The quality increases with depth and varies across the vein due to the gangue minerals sandwiched within the barite ore. However, the specific gravity of barite ore is improved by adopting efficient processing methods to remove gangue minerals (impurities/undesired minerals) from the ore. Such beneficiation techniques include crushing, screening of particulates, enrichment, upgrading, and handling materials. This series of processes ease the liberation of valuable minerals when the barite is comminuted. In most specialized operations, various distinguishing properties of the minerals such as magnetism, wettability, and density are employed during barite processing. This solely hinges on the ore's grade, the projected application of the minerals, nature of gangue, and liberation size. Most importantly, heavy media separation and jigging are generally employed on high-grade and coarsely liberated ores, while gravity concentration techniques are adopted to produce intermediate concentrates. Similarly, flotation is followed where the ore is finely comminuted (Chen et al., 2019; Cilek & Karaca, 2015; Grigorova & Nishkov, 2016; Hadjiev et al., 2000; Martins & Ausaji, 2011; H E Mgbemere et al., 2018; Henry E Mgbemere et al., 2011; Raju, Ananda, et al., 2016; Sampaio et al., 2016; Ulusoy & Yekeler, 2007; Zhao et al., 2014)

2.7 History and Background of Mining in Nigeria

Organized mining in Nigeria started in 1903, and around 1939, privately owned foreign companies were fully involved with mining minerals. This progression in mining activities necessitated regulations, such as the Minerals Ordinance and Coal Ordinance, enacted in 1946 and 1950, respectively (David Oluwasegun Afolayan, Onwualu, et al., 2021; MMSD, 2010). These enactments provided the base for establishing various government agencies, leading to their reviews in 1999. However, the advent of oil discovery in 1958 and energy crisis in the 1970s resulted in the collapse of big mining companies and massive unemployment of mine workers. Many of them went into illegal mining activities, having seen the hopelessness of diversifying the nation's economy (David Oluwasegun Afolayan, Adetunji, et al., 2021; David Oluwasegun Afolayan, Onwualu, et al., 2021; Abraham Ighoro Ebunu et al., 2021; Otoijamun et al., 2021).

As part of the Nigerian government effort, the Mining Cadastral Office (MCO) was created to administer mining titles, to oversee the enactment and enforcement of the Nigerian Minerals and Mining Act of 2007, National Mineral and Metals Policy of 2008, and the Minerals and Mining regulations of 2011 (David Oluwasegun Afolayan, Onwualu, et al., 2021; MMSD, 2010). However, the official and prompt response to the illegal mining and unregulated mineral extraction in the mining industries was wild yet not sustainable. Unregulated mining activities have continued to flourish due to the ineffectiveness of the relevant agencies and lack of alternative gainful employment (D.O. Afolayan, 2017; David Oluwasegun Afolayan, Onwualu, et al., 2021). Research has emphasized that mining involves mine development, mineral extraction and smelting, re-mining, and waste management. It is a process through which man earns minerals from the earth and turns them into valuable goods for his use (Alokolaro, 2012; Warhurst, 1994).

2.8 Artisanal and Small-scale Mining Operation

Artisanal mining characterizes barite mining in Nigeria. Generally speaking, artisanal and small-scale mining is done by individuals, groups, families or cooperatives with minimal or no mechanization, often in the informal (unregulated) sector of the economy. However, this activity turned into a well-paid business before the abandonment of the mechanized mining method in the 80s (Mallo, 2012; MMSD, 2010). Since then and to the present, the exploration and exploitation (extraction) of baryte in Nigeria has been manually characterized by using primitive tools such as hammers, chisels, diggers, and shovels, usually on a small scale (David Oluwasegun Afolayan, Onwualu, et al., 2021; Ahmed & Oruonye, 2016; Macdonald et al., 2014; Mallo, 2012; Melodi & Opafunso, 2014; Oramah et al., 2015; Otoijamun et al., 2021). Under these circumstances, indeed, only the surface or near-surface veins are exploited, while local miners' work is hazardous, resulting in the loss of lives and property (David Oluwasegun Afolayan, Onwualu, et al., 2021; Mallo, 2012; Warhurst, 1994).

The baryte exploitation within the Benue Trough is done indiscriminately either by individuals or groups. Nevertheless, there appears to be some coordination in how each individual or group goes about the exploitation (David Oluwasegun Afolayan, Onwualu, et al., 2021). The environmental impact and devastation of arable farmland are significant, in addition to the presence of very large and deep pits left behind after exploitation which could form death traps (Adamu et al., 2014; David Oluwasegun Afolayan, Onwualu, et al., 2021; Chaanda et al., 2010; Drochioiu et al., 2016; Hatar et al., 2013; Ikpi et al., 2021; Sunday et al., 2018). On a positive note, artisanal and small-scale mining in Nigeria is a significant sector that can provide a livelihood for millions of people and produce a sizeable proportion of the world's extractive commodities. It is an important sector to the international community, providing substantial benefits to efforts focused on reducing poverty and stimulating economic growth. This is necessary for political and economic stability, especially to solid mineral endowed developing nations such as Nigeria and other Africa countries (David Oluwasegun Afolayan, Onwualu, et al., 2021; Ibrahim et al., n.d.; Mallo, 2012; Otoijamun et al., 2021).

2.9 Basics in Baryte Processing

2.9.1 Introduction

The basis and practice of minerals processing are as old as human civilization itself (METSO, 2018; MMSD, 2010; Omotehinse & Ako, 2019). It involves the reduction of the mine ore and removing the gangue accompanying the ore. This clearly describes the act of producing the ore to obtain a mineral through prospecting, exploitation, development, exploration, and reclamation with the application of geochemistry, geobotany, geophysics, and geotechnical fields. It forms the central division of extractive metallurgy referred to as beneficiation. Baryte is commonly beneficiated by using physical separation techniques like crushing, screening, log washing, jigging, heavy media separation, tabling and spiral concentration, magnetic separation, and in some cases by selective flotation. However, beneficiation strategies largely depend on the grade of the ore, the nature of the gangue minerals, and liberation size (D.O. Afolayan, 2017; H E Mgbemere et al., 2018; Henry E Mgbemere et al., 2011; Nwoko & Onyemaobi, 1997; Nzeh & Hassan, 2017; Raju, Ratchambigai, et al., 2016; Zhao et al., 2014).

Baryte processing aims to recover value minerals (barytes and other desired minerals) from other undesired minerals within the barite rocks or ore. Baryte processing produces the maximum value from barite ore. This can be in form of crushed products with specific sizes and shapes or complete recovery of barite minerals from the overburden and other gangue minerals. The technologies and methods of achieving these goals are conventional, complementary, specific, and well defined. The different stages in barite processing are the following.

1. Blasting (drilling): Explosives are used to blast rock or stone formations (D.O. Afolayan, 2017). There are other manual methods or mediums of expanding and cracking rocks by applying wood fuel, horn-out tires, or combining any processes to heat the barite vein (D.O. Afolayan, 2017; METSO, 2018).
2. Crushing and screening: This first controlled size reduction stage (FCSRS) controls other aggregate production and preparation processes for further size reduction (Adiawe, n.d.).
3. Grinding: The liberation sizes for barite and other associated gangue minerals are reached at the stage of size reduction where further size reduction filler (micronized form) is produced. This can be achieved for both wet and dry processing techniques.
4. Slurry and Pyro processing: These apply technologies for the wet processing of minerals, enrichment, and upgrading the mineral fractions by drying and calcining.
5. Materials handling and Compaction: The fully enriched and upgraded baryte mineral are further processed before milling. In doing this, the minerals are densified, impacted, and pressurized to ensure maximum recovery of pulverized or comminuted baryte ore from

the mill during comminution (D.O. Afolayan, 2017; METSO, 2018). Technologies and devices are employed in moving the process flow of materials via loading, transportation, storage, and feeding. These are fully accomplished during the blasting, primary crushing, and materials handling operations in open or underground pits, as clearly shown in Figure 2.3 (METSO, 2018).

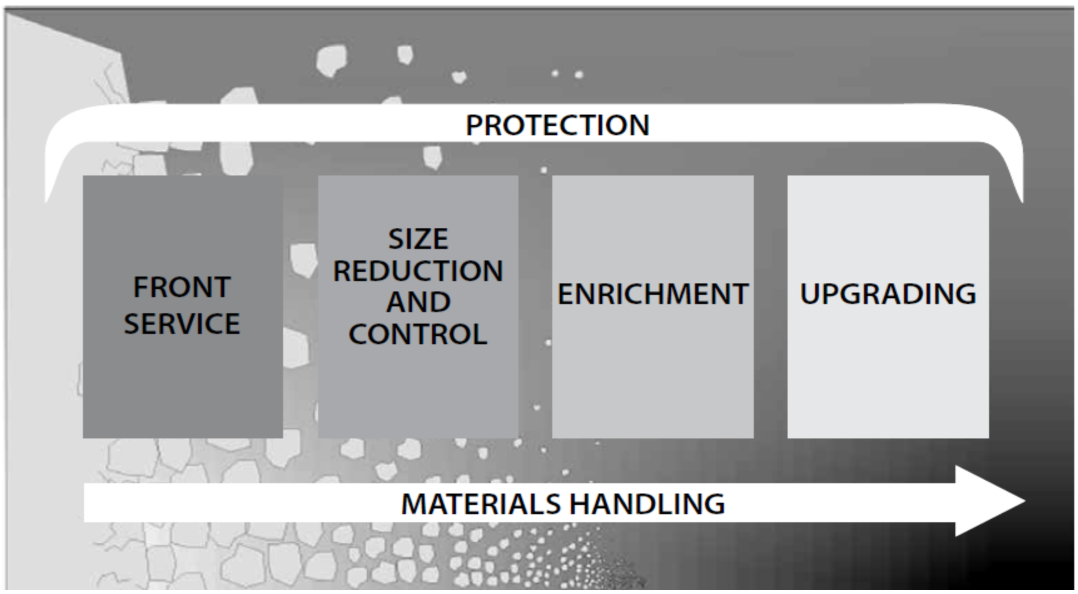

Figure 2.3: Processing techniques and mine pits (METSO, 2018)

2.9.2 Operation Stages, Size Reduction and Control, Screening, and Classification of Barite Ore

Operation Stages and Size Reduction of Barite Ore: This is the largest process operation in processing baryte minerals with the goal to produce mineral fractions that ease the liberation and recovery of the barite mineral from other gangue minerals. The appropriate liberation size of barite mineral from the gangue (non-barite minerals) contained in the host rock is generally in the interval of 10 – 100 micron. Liberation analysis of baryte ore has shown that ~98% to ~100% of baryte and gangue minerals are free or liberated, and ~ 2% of the value minerals are interlocked. However, crushing and grinding the run-of-mine (ROM) or barite ore is necessary to maximize the recovery of value mineral. This is achieved by applying screens and a spiral classifier for the coarse and finer part. These comminution techniques are combined to improve the size fraction of the minerals at the process stages and in the final products (METSO, 2018).

Crystals of baryte ores break into different sizes and shapes upon the application of energy during crushing and milling processes. The entire process is efficiently controlled by the selecting appropriate equipment needed for size reduction, and optimizing conditions such as reduction ratio, reduction techniques, and feed size to achieve desired comminuted products. The number or quantity of oversize and under sizes produced at the end of the size reduction process and the quantity of fines in the pulverized baryte ore are reduced significantly. Moreover, the operations in size reduction are dictated by the feed characteristics of the ore, the crushing parameters such as the crushability or grindability (work index), and the wear rate (abrasion index) (METSO, 2018). Other size-controlled methods such as screening and classification are achieved through a geometrical pattern and particle motion, respectively. This happens in a typical barite processing plant or mining site and the screening process is done by stratification or mechanical sieving. The process is the same for laboratory-scale mineral processing, where a little quantity of small-particle size barite ore is classified into different size ranges before processing. Thus, the conditions favour each stage of the entire process are defined and considered in process and equipment design phases (D.O. Afolayan, 2017; METSO, 2018). Figure 2.4 shows a pendulum pulverized miller through the bucket elevator to the product silo.

(a) (b)

Figure 2.4: Pendulum pulverized Mill and Jaw crusher in a crushing Site at Benue State (D.O. Afolayan, 2017)

2.9.3 Enrichment, Upgrading, and Mechanical Dewatering of Barite Mineral

2.9.3.1 Enrichment of barite Minerals

The removal of impurities (clay minerals, light and fine particles of minerals) and other gangue minerals (galena, sphalerite, hematite, and calcite) from barite minerals improves the value and the quality of the mineral. This is achieved by washing and separating products either in solid or liberation particle form. In a typical barite mining and processing plant (PIN Ltd), wet screen and tumbling scrubbers were considered for the enrichment process over the log washers, aquamator separator, and attrition scrubbers. The selection was based on the availability of processing equipment (D.O. Afolayan, 2017; PIN, 2017). The leaching method of separation for wet processing techniques is mostly considered over gravity or magnetic separation and floatation for the particle sizes. For the damp screen, the water spraying washes baryte regardless of the hole size in the screening media. On the mining site, a tumbling scrubber or a speedy washing drum for scrubbing solids is also used to wash barytes minerals which contain a high and sticky content of clay and dirt, as shown in Figure 2.5 (D.O. Afolayan, 2017). In addition to these techniques, dense media separation may be introduced to recover baryte mineral from the mix of heavy gangue minerals such as galena and hematite with a density difference of 1.75 and above, for a mineral size range of 100 microns and below (D.O. Afolayan, 2017; PIN, 2017).

.

(a) (b)

Figure 2.5: Heaps of Barite ROM, manual and mechanized enrichment techniques (D.O. Afolayan, 2017; PIN, 2017)

2.9.3.2 Upgrading and Mechanical Dewatering of Barite Mineral

The upgrading of final products is the goal of barite processing. It involves processes of improving the production values of the concentrate. This is achieved by converting the concentrates into a dehydrated form, either through calcination or sintering, to efficiently recover valuable minerals from the tailings. Similarly, barite minerals of fine or small particle size are recoverable through mechanical removal of liquids from slurry to obtain solids in a suitable form. The fine particle mixtures of baryte and other gangue minerals are packed into the sack with the shovel. Barite aggregates are hand-picked from the mix of tailings recovered after washing, as shown in Figure 2.6. The drained slurry is allowed to dry under the sun's heat for a few hours to enable the recovery of baryte (D.O. Afolayan, 2017; METSO, 2018).

(a) (b)

Figure 2.6: Enrichment and upgrading of barite and other associated gangue minerals (D.O. Afolayan, 2017; PIN, 2017)

2.9.4 Materials and Slurry Handling, Wear of Equipment and Protection in Baryte Processing

2.9.4.1 Materials and Slurry Handling in Baryte Processing

This is the climax in barite processing, where the process stages of size reduction, size control, enrichment, and upgrading the core values of the minerals are brought to the attainable optimum. On a laboratory scale, by jigging, pulverized baryte ore is dispersed in water feed into the jigging column. The slurry (jigging products) is decanted to separate water from the wet solids. The solids (concentrate and tailings) are oven-dry and characterized. In large-scale barite processing, technologies and equipment for loading and unloading, storing, feeding, and transportation are required to achieve complete and comprehensive processing with minimal disturbances.

Baryte and other gangue minerals such as galena and zinc are separated into bags for weighing and transported into the store through a wheelbarrow (D.O. Afolayan, 2017; METSO, 2018). Similarly, baryte minerals are transported by the conveyor belt, upon which the ROM is prepared for enrichment moves. The materials are conveyed from the feeding plate (trommel), the washing drum, and the product plate.

2.9.4.2 Heavy Metal Contamination

The groundwater, which is a significant source of freshwater within the mining areas, is distributed based on the volume of rainfall, streamflow, weathering and mining activities, and the texture and structure of the rocks. Mining excavations, drilling, and open and blasted wells create direct access to groundwater. They are contaminated by the oxidation of abandoned mine tailings, leaching of heavy metals, and drainage of materials from active and abandoned mines (David Oluwasegun Afolayan, Onwualu, et al., 2021; Gabriel et al., 2020). In a typical mining site, water used in washing the ore is returned into the mined pits and flowing rivers. Similarly, packets and aggregates of barite stones fall off the truck and are dispersed on the soil and rivers. These solids are carried by water as sediments around the river beds, settle and contaminate water for drinking and other domestic purposes. Depending on the concentration of heavy metals present in water, miners and the mining community are exposed to a certain level of risk imposed by mining which may be acute or chronic over a long time (Adekoya, 2003; Ankidawa et al., 2020; Diloha et al., 2018; Gabriel et al., 2020; Nzeh & Hassan, 2017; Raju, Ratchambigai, et al., 2016).

2.9.5 Emerging Investment Opportunities in Barite Processing

As a well-endowed nation, Nigeria has vast deposits of mineral resources at different levels of exploration in its local government, and some are yet to be discovered. There are unparalleled opportunities for professionals, scientists, and researchers with relevant skills to engage in mineral prospecting and exploration. However, baryte minerals are exported as raw materials in their crudest form without adding value through beneficiation or processing. This has resulted in the loss of revenue for the country. There exist overwhelming abundant opportunities for mineral beneficiation in Nigeria.

Similarly, an efficient barite processing strategy is the surest route to self-sufficiency in oil drilling and massive industrialization of the entire petroleum industry (Alokolaro, 2012; MMSD, 2010). Several foreign and indigenous mining industries use barite as primary raw materials. Investing in baryte mining and processing in Nigeria is timely. Many ambition and employment are expected alongside the mining sector value chain. Similarly, Lawyers, Risk Analysts, and Business Service Consultants, medical practitioners, and financial institutions must support new companies entering the market with robust and bankable business plans, realistic feasibility studies, and market research.

2.9.6 Uses, Pricing, and Availability of Baryte

❖ Specification and Uses:

1. The primary and global use of barite is as a weighting agent in oil and gas well drilling mud. Baryte in micronized form is added to the drilling mud to increase the density of the fluid column above the drill bit to prevent a blowout. Although there are alternatives, baryte is the preferred weighting agent. It is non-corrosive, non-abrasive, insoluble, and non-toxic. It is also relatively cheap and readily available (David Oluwasegun Afolayan, Adetunji, et al., 2021; Bonel, 2005; Strachan, 2010).
2. Baryte has a high density, low solubility, high brightness and whiteness, chemical inertness, softness, and relative cheapness also makes it of great value in many other applications. These unique uses include:

- As sustainable filler in paint and plastic and as the primary source of barium for the chemical industry. Processed baryte in the form of barium metal can remove traces of gases in vacuum tubes.
- Barite serves as raw materials for the production of lithopone (high-performance white pigment composed of a mixture of chemically precipitated and calcined zinc sulphide and barium sulphate).
- Barite may be added to concrete to increase its density for specialist application. Also, it finds application as an absorber of gamma and X-ray radiation.
- Used as a flux, which adds brilliance and clarity during glass manufacturing (Bonel, 2005; Brobst, 1958; Ngukposu A Labe et al., 2018b).

Currently, the world is moving away from fossil fuels into electric batteries and other renewable energy sources for automobiles and to drive engines. The use of baryte in oil and gas drilling operations will likely decline. Aside from the demand for API drilling grade barite, the use of barite grades such as the chemical grade, micronized white grade, precipitated barium sulphate, and white barite grade in different applications requires the same basic mineral processing methods. Thus, advanced technologies and devices are required to diversify the use of barite ore reserves or deposits of Nigeria into other areas of need and significance.

2.10 Drilling Operation and Fluid Technology

A hole or oil reservoir is drilled hundreds of meters into the rock formation to capture the oil and gas and bring them to the surface. This operation is held many feet in an underground reservoir at high pressure and temperature. The temperature and pressure of a reservoir are depth-dependent. The hydrostatic /reservoir pressure increases at 0.376-0.39 Psi per feet and the temperature at 0.6 ^{o}F -1.6 ^{o}F per 100 feet (Joel, 2013). Baryte is used as a weighting agent in the oil drilling fluid required for drilling operation. It exerts pressure by its weight maintained slightly higher than the hydrostatic pressure of the overlaying water (Baroid, 1997; Strachan, 2010; Thomeer & Bottema, 1961). The drilling fluid is necessary to control pressure in the oil well during drilling and prevent blowout.

In addition to barite, a mixture of clay, oil-field chemicals, either water, oil, or a mixture of oil and water. The types and composition of drilling fluids used daily depend on the oil well and the hole. Drilling fluids are selected, maintained, and related directly or indirectly to most drilling problems. Thus, barite used as a weighting material in drilling fluid is processed to meet the American Petroleum Standards (API) and ensure oil drilling to the surface (Breuer et al., 2004; Holdway, 2002; Neff, 2005). Table 3 shows the standards and material properties of drilling grade barite. The density of baryte increases the weight or density and solid volume of the drilling fluid. It is necessary to suppress the formation pressure. The water soluble salts improve the rheology of the fluid. Different particle size fractions contribute to the quality of the fluid, the filter cake, and rheology (fluid flow). The presence of heavy metals and toxic chemicals such as cadmium, lead, mercury, flotation chemicals, and disodium pyrophosphate (SAPP) in barite is not acceptable. Thus, drilling grade baryte must meet the requirements or specifications stated in Table 3.

Table 3: Combined API/Company Barite Specification (API, 2004, 2009)

PROPERTY	UNITS	REQUIREMENTS
Density	g/cm^3	4.20 minimum
Water Soluble Alkaline Earth Metals as Calcium	mg/kg	250 maximum
Residue greater than 75 micrometers	% w/w	3.0 maximum
Particles less than 6 micrometers in equivalent spherical diameter	% w/w	30 maximum
Particles less than 4 micrometers in equivalent spherical diameter	% w/w	20.0 maximum
C. E. C	meq/10gms	0.18 maximum
Extractable Carbonates	mg/kg	3000 maximum
Cadmium	mg/kg	5 maximum
Lead	Mg/kg	1000 maximum

Mercury	Mg/kg	5 maximum
Moisture Content	% w/w	1.0 maximum
Flotation Chemicals	% w/w	Zero
Hematite	% w/w	Zero
SAPP	% w/w	Zero
Other: The presence of sand can be observed under a microscope. Additional properties may be determined according to API standardized test procedures (Reference RP 131, June 1, 1995, for the following controls: • The abrasive capacity of the weighting agent • Presence of mercury, cadmium, and lead		

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3.0 CHAPTER THREE: CHARACTERISATION OF BARYTE RESERVES IN NIGERIA FOR USE AS WEIGHTING AGENT IN DRILLING FLUID

3.1 Introduction

Over 80% of baryte produced worldwide is used as a weighting agent in drilling fluids. World barite resources are about 2 billion tons, but only 740 million metric tons have been identified. China, India, Kazakhstan, Morocco, Thailand, USA, Turkey and other countries produced 9.5 million metric tons in 2018, worth 2,688 million US dollars. Brown barite, residual deposit type barite, baryte 4.3, and oil and gas industry barite market generated revenue of 806.4 million US dollars, 860.2 million US dollars, 645.1 US dollars, and 564.5 US dollars, respectively. Baryte is used for drilling and other industrial applications worldwide (Garside, 2020; MMSD, 2010; Researchdrive, 2020). Nigeria in Africa currently holds the fourth largest baryte deposits in the world, with an estimated reserve of over 21 million metric tons. Ironically, the nation is not on the list of globally recognized largest baryte producer for drilling activities and other industrial applications (Garside, 2020; MMSD, 2010). Principal factors responsible for this include the unregulated importation of unprocessed barite ore, limited access to the mining site and high-quality baryte ore grade, absence of mechanized mining companies, unregulated artisanal and small-scale mining (ASM) activities, and lack of industry-institution-government collaboration among the oil and gas industries, research institutes and local barite producers (MMSD, 2010).

There are low, medium and high-quality barite in Nigeria, as shown in Table 3.1 and Figure 3.1 (Minerals and Industry in Nigeria, 1957; Oden, 2012). The mining of barite between 0-5 m depth gave rise to low-quality baryte due to associated impurities and low-pressurized hydrothermal fluids deficient in $BaSO_4$. However, further studies on some barite deposits have shown that mining barite deposits below 15 m depth produce medium to high-quality grades of barite (MMSD, 2010; Oden, 2012; Onwualu et al., 2013). In addition, some considerable research and exploration studies report on the low, medium, and high-grade with the recommendation that further processing is necessary to upgrade the potential of few identified high-grade deposits (Labe et al., 2018; H E Mgbemere et al., 2018; Henry E Mgbemere et al., 2011; Oden, 2012). Baryte ore requires upgrading to minimum purity, specific gravity, and composition with qualities needed in drilling and other industrial activities (MMSD, 2010; NGSA, 2010). This can be achieved at a reduced cost when beneficiation is done at or near the mining site using basic and efficient processing methods (Tanko et al., 2015). However, barite's on-site beneficiation is a pre-processing approach and is insufficient to upgrade low-quality barite ore to the American Petroleum Institute (API) standard.

Table 3.1: Quality Variation of Barite deposits in Nigeria (David Oluwasegun Afolayan et al., 2021; MMSD, 2010; NGSA, 2010; Oden, 2012; Onwualu et al., 2013)

Low Quality (SG: 3.0-4.0)	Medium Quality (SG: 4.0-4.2)	High Quality (SG: Above 4.2)
Aloshi, Azara, Wuse,	Ribi, Afuze, Ambua	Ibi, Afuze, Alifokpa
Pupule, Mubi, Apawa,	Ntak, Yandev, Pila-Tandev	Makurdi, Bundin-Kwaj-ali
Tombu, Bunde Lessel,	Lessel, Obubra, Kornya	Igara, Yala, Afugo, Guma
Port Harcourt, Lessel	Kumar, Ihugh, Azara,	Gabu, Osina, Konshisha
Kuduku, Obubra, Keana,	Guma, Orgba, Mayo-Belwa	Didango, Kumar, Torkula

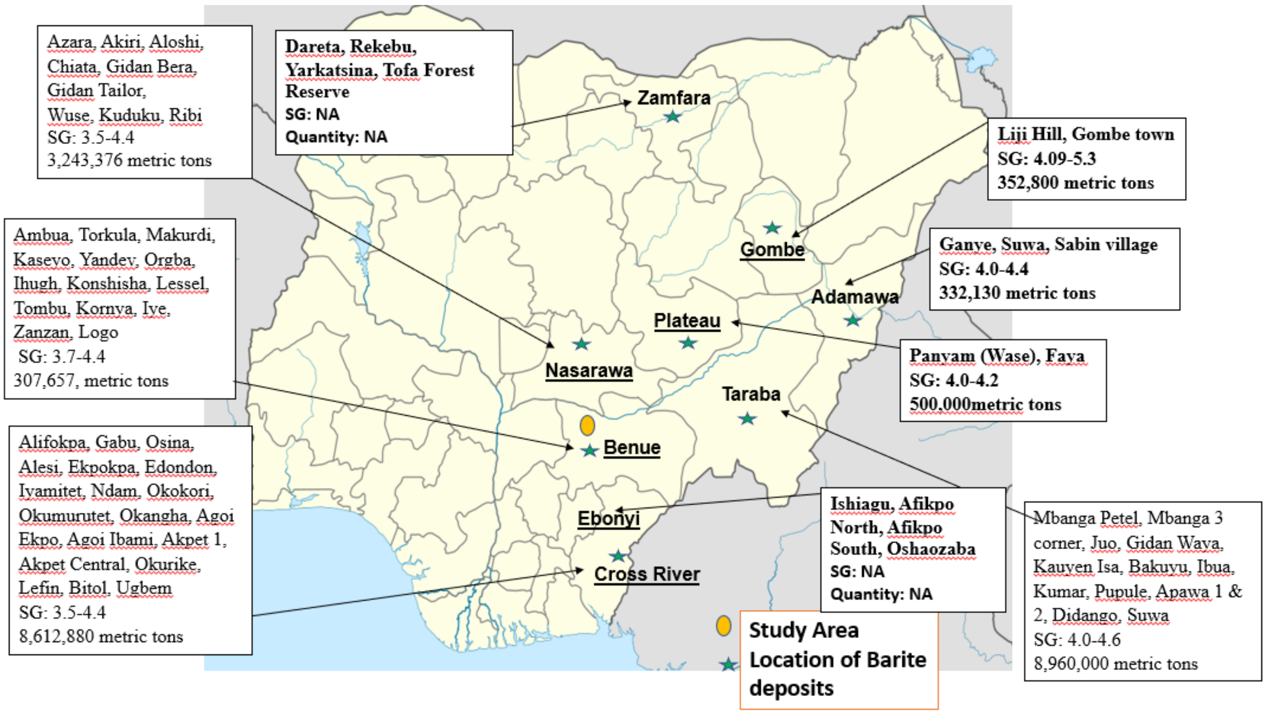


Figure 3.1: Barite deposit map of Nigeria showing the locations, quality, and reserve estimates *(D.O. Afolayan, 2017; MMSD, 2010; NGSA, 2010; Onwualu et al., 2013)*

The demand for high-quality barite as a drilling fluid weighting agent has been increasingly difficult to meet due to variation in the level and form of gangue minerals in the ore. The operations of local barite processors, and the use of gravity separation, chemical leaching, and flotation techniques to upgrade barite quality have been explored and reported in the literature (Achusim-Udenko, A. C. Gerald, O. Martins, O. and Ausaji, 2011; Chen et al., 2019; Grigorova & Nishkov, 2016; Liu et al., 2019; H E Mgbemere et al., 2018; Henry E Mgbemere et al., 2011; Nzeh & Hassan, 2017; Raju et al., 2016; Wang et al., 2014; Zhao et al., 2014). However, these reports do not show much evidence on specific methods for evaluating or performing local processing methods of barite in Nigeria to reveal the local product's quality and present a parallel comparison between the industrially accepted barite imported from Morocco and local products. The environmental concern posed by flotation and other adhering chemicals and the elimination of water-soluble salts of Na, K, Ma, and Ca in baryte due to acidic leaching were not considered.

Field experiments of small-scale processing that reflect the practice of barite processing locally need to be done to leverage the laboratory-based experiments as shown in previous studies in Table 3.2 to translate theory into practice. Furthermore, the requirements or standards for weighting agents in drilling mud exceed just specific gravity needs, which were the major focus of research works as presented in Table 3.2. There are physio-chemical properties that determine the rheological properties of the drilling mud. Predominant surface mining of baryte contributed to the low-quality stigma of mined products in Nigeria. However, it is essential to show the extent to which the local product is inferior or superior to the industrially accepted barite imported from Morocco and to indicate steps that should be taken to reverse the trend of excessive importation of barites.

Table 3.2: Previous studies on barite processing

Main parameters studied	Main Results	References	Research Findings
Froth flotation and chemical Leaching of +180 µm, (-180+90) µm Azara baryte Using pine oil, oleic acid, HCl, and HOCl	Increased barite SG from 3.207 to 4.38, 64.6% $BaSO_4$ to 99.5% $BaSO_4$.	(Henry E Mgbemere et al., 2011)	Eliminate water-soluble salts of Ca, Mg, Na, K needed for the rheology of drilling fluid and Filtration control in drilling application.
Lab-based jigging and froth Flotation of (-350+180) µm Size Azara baryte using NaOH and oleic acid	increased baryte SG from 3.72 to 4.23 at 92.9% recovery	(H E Mgbemere et al., 2018)	Environmental concern due to the discharge of used chemicals. Effect of the adhering chemicals on baryte surface and its consequence on barite sag.
Lab-based combined Jigging, tabling gravity Separation and HCl& H_2SO_4 of (-350+250) µm Size Azara baryte	Increased baryte SG from 3.85-4.46	(Nzeh & Hassan, 2017)	Research work limited to laboratory study and not implied the reality on the mining fields.
Flotation recovery of Azara Baryte using locally processed palm bunch Palmitic acid, sodium Silicate, KOH, and H_2SO_4	Upgrade baryte concentrate from 75.4% to 91.9%	(Achusim-Udenko, , A. C. Gerald, O. Martins O. and Ausaji, 2011)	High material loss (5.5% to 8.1%) High material loss (15.6%)
Lab-based flotation of pure Artificially mixed fluorite And Chongquig barite using NaOL, modified starch, HCl, and NaOH	Increased baryte recovery from 89.62% to 91.16% using NaOL	(Chen et al., 2019)	It is a separation of artificially-mixed barite-fluorite system and not naturally occurring ore
Laboratory and -	Increased baryte	(Raju et al., 2016)	Nearly 50% baryte lost in tailings

Commercially-based Flotation of Mangampet Bartte using Armoflote-17, Liquid B-50, and Sokem-524C (a vegetable oil-based amine Collector) in a flotation column	assaying from 82% to 94%-97%	due to the ineffectiveness depression of barite by starch

Barite importation in Nigeria represents 3.6 % of total industrial minerals importation with an estimated consumption of 440,000 metric tons for 2020 and valued at 96 million US dollars. Although there has been an existing policy on the ban of barite importation since 2011, the government cannot effectively enforce this until the local barite supply chain can guarantee a sustainable supply of the commodity. However, to close the demand-supply gap, the Nigerian government has taken steps to reverse importation (MMSD, 2010). These steps can only succeed if scientific data and information enable informed decisions to regulate stakeholders along the barite value chain. The present work is designed to give scientific support to the efforts. This includes the Raw Materials Research and Development Council, Nigerian Local Content Monitoring Board, Nigerian Geological Survey Agency, Federal Ministry of Mines and Steel Development, activities by the private sector such as Barytes Miners, and Processors Association, TOTAL Plc, etc.

In this research, the local processing of barite was presented. The physio-chemical properties of the crude and on-the-site processed barite were measured and compared with imported barite and API standards. The locally processed barite was examined for suitability as a weighting agent additive in drilling fluid. Recommendations were made to develop and optimize processing methods that will enhance the quality of locally processed baryte to compete favourably with barite products in the global market used for different drilling activities in the oil and gas industry. The manuscript, in a nutshell, seeks to provide relevant scientific information to support efforts of some government agencies and the joint committee on baryte processors-oil producing companies in Africa on the value addition of barite deposits in the Middle Benue Trough of Nigeria.

3.2 Research Methods

3.2.1 Location, Mapping, and Evaluation of Torkula Barite Deposits

The Benue barite reserves consist of Lessel barite and Guma barite fields. Lessel field in Benue State has many veins and occurs mainly in the south of Gboko (all through the Yandev deposit North of Gboko), Lessel Bunde, Lessel Mbato, and Lessel Mbagwa. Currently, there are more than 20 veins in production. Similarly, the Guma field consists of vein deposits in Iye, Kaseyo, Zanzan, Makurdi, and Torkula-Hungwa axis. The highest concentration of barite veins in the area is within the Torkula-Hungwa axis. Although the number of known veins in the axis is currently fewer than in Azara, and Kumar, its barite deposits hold a lot of promise. Recent field work at three veins revealed that the third vein is massive and has produced thousands of tons of barite with a specific gravity above 4.2 (D.O. Afolayan, 2017; Oden, 2012). This is presented in Table 3.1. Aside from the fieldwork, there is little to no research on barite deposits within the Torkula-Hungwa axis other than the mineral mapping carried out by the Nigeria Geological Survey agency on behalf of the Polyguard Investment Nigeria, Ltd (D.O. Afolayan, 2017).

Torkula baryte deposit is located in the Guma local government area in the Benue State of Nigeria and has a total landmass of about 28,882km^2 as shown in Figure 3.2. It is surrounded by sedimentary rocks, and the soil is dominantly associated with mineral deposits like lead, salt, baryte, feldspar, and brown earth of volcanic origin. Guma lies between latitude N7 32 and N8 51 and longitude E9 35 and E9 22 with an average high rainfall of about 1198 – 1798mm annually. The relative humidity is between 43% and 86%, and temperature ranges from 27^{o}C and 37^{o}C. The highest concentration of baryte veins in this field is within and around Torkula because of its size. However, there is a baryte quality contrast between the top and lower portions of the vein. This disparity is due to major impurities such as quartz, iron oxide (goethite), fluorite, and carbonates of iron, calcium, and magnesium. (API) (API, 2004, 2009; Fatoye et al., 2014).

Figure 3.2: Torkula in Guma Baryte Field, Benue State, Nigeria

3.2.2 Sampling and On-the-Site Beneficiation of Baryte

The mining of barite in the Torkula baryte field is done on a large scale. Soil overburden deposits are removed from the surface of baryte veins and explosives are used for the fragmentation of the barite rocks. With the aid of an excavator and a loader, the blasted run-of-mine (baryte ore) is removed from the pit of about 35 m deep and loaded into a truck. Heaps of baryte ore, mixed with impurities. Also, local processing (on-site beneficiation) and screening of processed baryte at Torkula-Hungwa barite field. Baryte and non-baryte minerals in the baryte ore are separated under the influence of gravity. This was done by applying pressurized water pumped from the mined pit on the baryte ore in a 2 m by 2 m wooden box. However, the pump pressure is reduced at the upgrading stages to allow complete sedimentation of minerals based on specific gravity differences. As the water flows over the barite ore, barite and non-barite minerals are separated/handpicked and kept in separate bags.

Baryte samples were randomly collected from the heaps of barite run-of-mine. White baryte was separated from the brownish, reddish and other coloured barite mineral (believed to contain non-baryte minerals), collected into cellophane bags (black polythene bag) and appropriately labelled. Since the heaps have been separated, it is believed that the materials from each heap are from similar depths. Collected samples were categorized into solid and milled samples. Similarly, the solid samples were labelled as solid samples A, B, C, D, E, and F. Solid sample A is white coloured barite with relatively small portion of sandstones, brown coloured barite was labelled solid sample B, different fractions of white and transparent barite samples as solid samples C and D. However, solid samples E and F were whitish with some associated gangue minerals interlocked within the barite vein.

For a comprehensive comparison and scientific criticism, research works on reference barite samples collected from Nigeria Petroleum Development Company (NPDC) Warri Field Office were cited. The air-tight barite samples selected from the Hungwa mining site were crushed and milled using a Jaw crusher combined with a Pendulum Pulverized Milling machine. On the other hand, milled or pulverized samples were labelled as unprocessed samples (Un. PS) A, B, C, D and on-site processed samples (On-SPS) as shown in Figure 3.3.

3.2.3 Sample Preparation

The crushed samples were sieved and screened with sizes ranging from 3 mm to 45 microns with a vibratory screen. This was achieved with the aid of a mechanical sieve shaker/size analyzer comprising an agitator coupled with a mesh of various sizes, ranging from 3 mm to 45 microns. The samples were poured gently into the upper sieve (sieve with the largest opening diameter) Other sieve have aperture sizes that are lower and are arranged in descending order to allow powder materials to separate into a similar particle size range. Samples are classified across the different mesh designations to collect the finest samples at the receiver plate. The sieving and screening were done to prevent the abrasion of casing during its potential usage by coarser grain particles during drilling (Ibe et al., 2016).

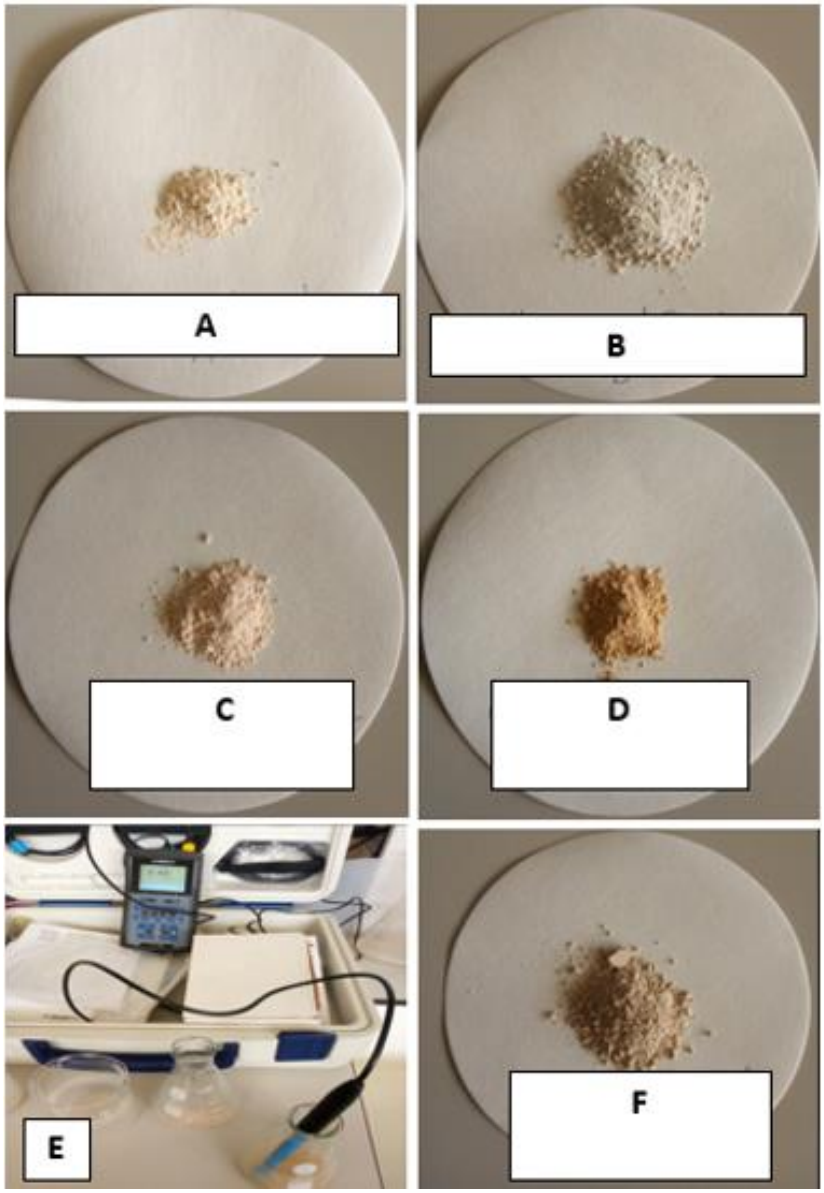


Figure 3.3: Sample preparation ((A-D) Different colours of unprocessed barite samples, (E) Experimental set-up for the pH measurement, and (F) the on-site processed barite sample)

3.2.4 XRD Analysis (phase analysis) of the Sample

The micronized samples of the crude and on-site processed barite minerals were analysed by the Bruker D8 Advance ECO A25 diffractometer with DAVINCI design. This was done on the reflection-transmission spinner stage using the Theta-Theta settings. The Two-Theta starting position starts from 15^{o} and ends at 80^{o} with a two-theta step of 0.0396 at 0.3 seconds per step. Energy requirement and details of the experimental procedure have been discussed extensively in the literature (Ayim & Enoch, 2009; Olusegu et al., 2015). Observable peaks obtained in the analyses were matched and analysed with the ICDD database. Files of d-spacing for hundreds of thousands of inorganic compounds are available from the International Centre for Diffraction Data as the Powder Diffraction File (PDF).

3.2.5 Determination of Sample pH

A 20 grams sample of the sieved baryte was placed in a beaker and 20ml of distilled water was added to it. The slurry formed was allowed to stand for 70 minutes and stirred for about 10 minutes, and the slurry pH was measured (Ibe et al., 2016). The electrode remained immersed in the sample slurry until the meter stabilized. The pH was measured repeatedly after 24 hours and specifically at the temperature range of 26.3^{o}C in line with the pH manufacturer's instruction manual (Ibe et al., 2016).

3.2.6 Determination of Metals

The samples were digested a the mixture of chloroform ($CHCl_3$) and 10% nitric acid (HNO_3). The metallic content of the digested samples was analyzed using atomic absorption spectrophotometer (AAS), Model: A-Analys 100. The liquid-liquid extraction method (LLEM) was employed in the absorption or digestion of the sample (Ibe et al., 2016).

3.2.7 Determination of Sulphate

The method of IITA (1979) was adopted to determine the sulphate in the sample. This was done in line with the recommended Specifications (Ibe et al., 2016).

3.2.8 Cation Exchange Capacity and Methylene Blue Absorption of Torkula Barite

A 2 ml sample of the baryte solution (baryte fluid) was drawn into the Erlenmeyer flask, 10 ml of deionized water and 15 ml of 3% Hydrogen peroxide (H_2O_2) were added to the drilling mud in the flask. Subsequently, 0.5ml of 5N H_2SO_4 was added into the mixture, heated and allowed to boil gently for 10 minutes. The mixture was diluted with deionized water to 50 ml mark, and methylene blue solution was further added to the mixture in drops. Furthermore, the content was swirled manually for a few seconds, and while the solids were still suspended, the glass rod was inserted into the solution. The tip of the inserted glass rod was placed on the filter paper, and the drop of the mixture was carefully observed. The swirling, observation and addition of more methylene blue solution drops were done continuous until a turquoise ring was seen on the filter paper (Burrafato, G. and Miano, 1993).

3.2.9 Determination of Sample Specific Gravity

The specific gravity of the sample was determined in accordance with the American Standards Testing Methods ASTM D854-00 (ASTM, 2015). Baryte stones/aggregate were screened into different particle sizes. Test methods for specific gravity of soil solids by water pycnometer was used to calculate the specific gravity of the 75 µm barite samples (a fully compacted material) at water temperature of 25 ^{o}C. The specific gravity of unprocessed barite ores (aggregates) was also measured.

3.2.10 Determination of Sample Moisture Content

Samples of 5 g, 10 g, and 15 g of the micronized barite were weighed into a dry and clean crucible and placed in an oven, working at an operating temperature of 105°C for 3 hours. At the end of the heating period, the samples were removed from the oven and kept in a desiccator, to cool for about 3 hours. The cooled samples were measured as the dried weight of the samples. The differential weights of the samples were compared and computed using an analytical weighing balance. The entire process was repeated after 3 hours until a constant weight was obtained (Ibe et al., 2016).

3.2.11 Determination of Sample Mohr's Hardness

Five (5) fully-enriched lumps (un-pulverized) baryte sample was scratched on the surface with the edge of a penny and an etched line was noticed. This was observed with the aid of a fingernail, to feel for a scratch and validate the nature of the scratch. If the barite is scratched, then it is softer than or equal in hardness to the test material, and if otherwise, it is harder than the test material. This method relies upon a scratch test to relate the hardness of a mineral specimen to a number from Mohr's scale (Alan, 1997). The scale was defined using an assembled set of common reference minerals of varying hardness and labelled these in order of increasing hardness from 1 to 10.

Similarly, the samples may also be scratched against either a knife, Coin, glass or finger nail. The observed results were evaluated on Mohr's scale of minerals hardness (Ibe et al., 2016; Omoniyi & Mubarak, 2014).

3.2.12 Determination of Sample Density (Mud Weight)

The required weight of the mud column establishes the density of the mud for any specific case. This is required as the starting point of pressure control of mud density and the balance of the formation pressure (Osokogwu, U., Ajienka, J. A. and Okon, 2014). The mud balance comprises a small vessel filled with mud and a metering section adjusted gently to account for the mud weight. This balance has two (2) different calibrations and was arranged according to the recommended Specifications (Omoniyi & Mubarak, 2014). The balance arm was positioned on the support base and was adjusted by moving the rider along the graduated scale until the level bubble was centred under the centre line. The density of the mud (mud weight) was measured and recorded appropriately. The cup outside was made cleaned and dry (Osokogwu, U., Ajienka, J. A. and Okon, 2014).

3.2.13 Effect of the Local Baryte on the Filtration Properties of the Mud

The effect of the local baryte on the mud filtration properties was investigated using a low pressure, low-temperature filter press. The presence of water in the filtrate indicates emulsion weakening, while thick filter cakes and high fluid loss indicate excessive drill solids content. The lid was removed from the bottom of the clean and dry cell and the O-ring placed in an undamaged groove to seal the inlet with a finger and prevent any mechanical damage. The cell was filled with the mud sample containing the local barite up to one-fourth (¼) of the O-ring groove, and a filter paper (Whatman No. 50 or equivalent) was placed on the top of the O-ring. The lid was placed on the filter paper with the flanges of the cell and turned clockwise until hand tight. A suitable graduated cylinder was placed under the filtrate opening to receive the filtrate.. This was done for 30 minutes according to API test specifications. The cell was disassembled and the mud discarded. The mud cake thickness was measured (Osokogwu, U., Ajienka, J. A. and Okon, 2014).

3.2.14 Effect of Baryte on the Rheological Behaviour of the mud

The formulated drilling mud (based on Table 3.3) was measured into the thermal cup up to approximately 70% and positioned on the viscometer stand. The cup was raised and stood until the rotary sleeve was wholly immersed in the scribing line on the sleeve, locked into place by a turning locking mechanism (Omoniyi & Mubarak, 2014). Dial reading was delayed or otherwise paused for 20 seconds to stabilize. The process was repeated for 600, 300, 6 and 3 rpm. Finally, the dial readings were observed and recorded according to the recommended API specifications (Osokogwu, U., Ajienka, J. A. and Okon, 2014).

Table 3.3: Different Formulations for Water-based Drilling Mud (Omoniyi & Mubarak, 2014; Osokogwu, U., Ajienka, J. A. and Okon, 2014).

S/N	Materials	Water-based drilling mud Formulations (Quantity)		
		Formulation (1)	Formulation (2)	Formulation (3)
1	Distilled Water (ml)	946.35	340.00	345.00
3	Barite (g)	20.00	10.00	5.00
4	CMC (g)	20.00		
5	Caustic soda (NaOH) (g)	20.00	2.00	1.00
6	Bentonite (g)	160.00	8.00	4.00
7	Pac-R (g)		1.00	0.50
8	Pac-L (g)		1.00	0.50
9	Xanthan gum (g)		1.00	0.50
10	Potassium Chloride (g)		10.00	5.00
11.	Soda Ash (g)		0.50	0.25

3.3 Results and Discussion

3.3.1 Phase Analysis of Torkula Barite

The X-ray diffractogram in Figure 3.4 reveals the composition and crystallographic information of the crude and on-site processed barite. Identifiable peaks in the diffractogram were matched with d-values obtained from the ICPDS card number 00-024-0020, and JCPDS (Joint Committee on Powder Diffraction Standards) data of card number: 39-222. Similarly, the crystallographic open database (COD) card number identified indicated the most dominant form of occurrence for the barium (in different phases) and sulphate as the most dominant elements. Other gangue minerals include quartz, calcite, and hematite. This is in line with reports given in literature (Aladesanmi, 2018; H E Mgbemere et al., 2018; Henry E Mgbemere et al., 2011; Tanko et al., 2015).

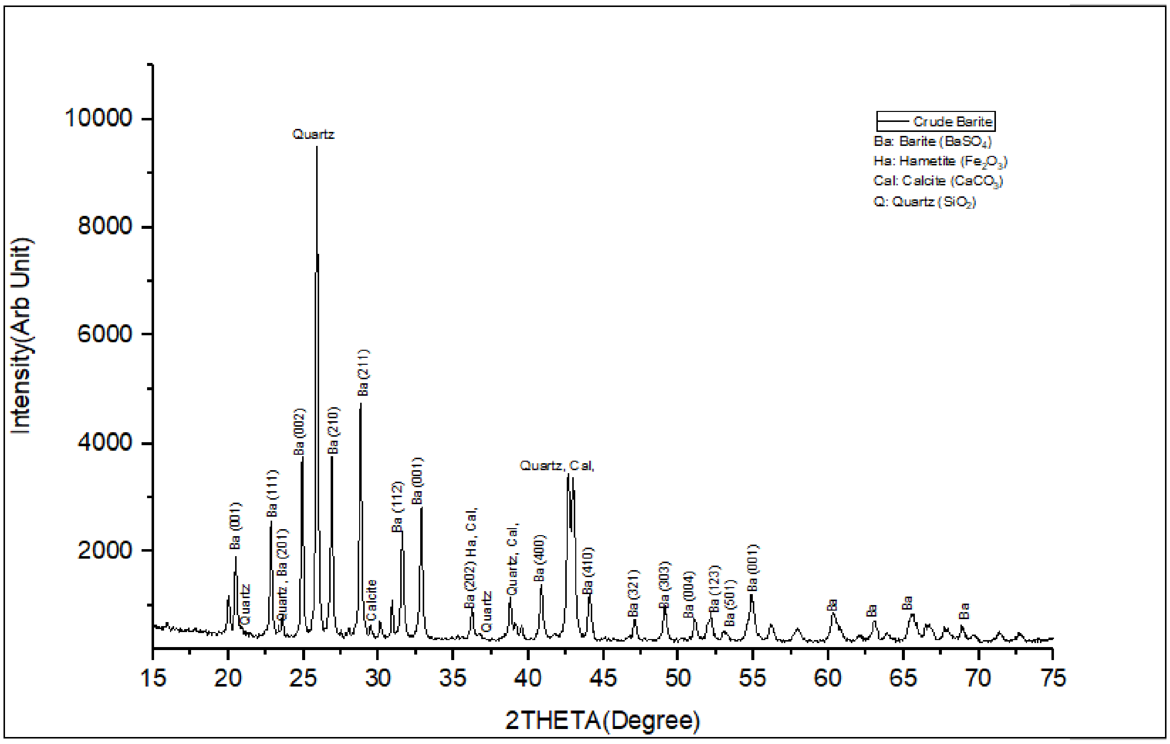


Figure 3.4: XRD pattern for Torkula barite from Guma LGA, Benue State

3.3.2 Assessment of the Chemical Composition and Properties of Torkula Barite

Table 3.4 shows that the on-site processed Torkula barite has 87.79% $BaSO_4$, 1.39% Fe_2O_3, 6.66% silicate salts, 1.603% total heavy metals, 0.589% CaO, 0.086% MgO, 0.75% Al_2O_3 and 1.10% LOI. The efficiency of the on-site beneficiation process adopted in Torkula baryte field justifies upgrading the materials characteristics of the mined minerals and enhancing the potency of the value addition strategies. Similarly, ICPMS and XRF results in Figure 3.5 and Table 3.4 indicate the presence of silica and alumina-based minerals (clay minerals), hematite and other heavy metals as the most dominant impurities. In contrast, other gangue minerals in traces include iron, potassium, zinc, strontium, and magnesium. However, the percentage of impurities in the Torkula baryte was low. Hence, the quality of Torkula barite can be upgraded to compete with high-grade baryte for oil drilling and other industrial applications.

Table 3.4: Elemental Evaluation of Torkula Barite

Composition	Percentage (%)	
	API Specification (API, 2010)	Torkula barite
$BaSO_4$	95.00	87.79
Fe_2O_3	0.03	1.39
CaO	0.01	0.589
MgO	0.04	0.086
Al_2O_3	0.035	0.75
Silicate	0.01	6.66
Total Heavy Metals	0.001	1.603
Water Soluble Salt	0.1	0.0301
Loss on Ignition (LOI)	0.5	1.10

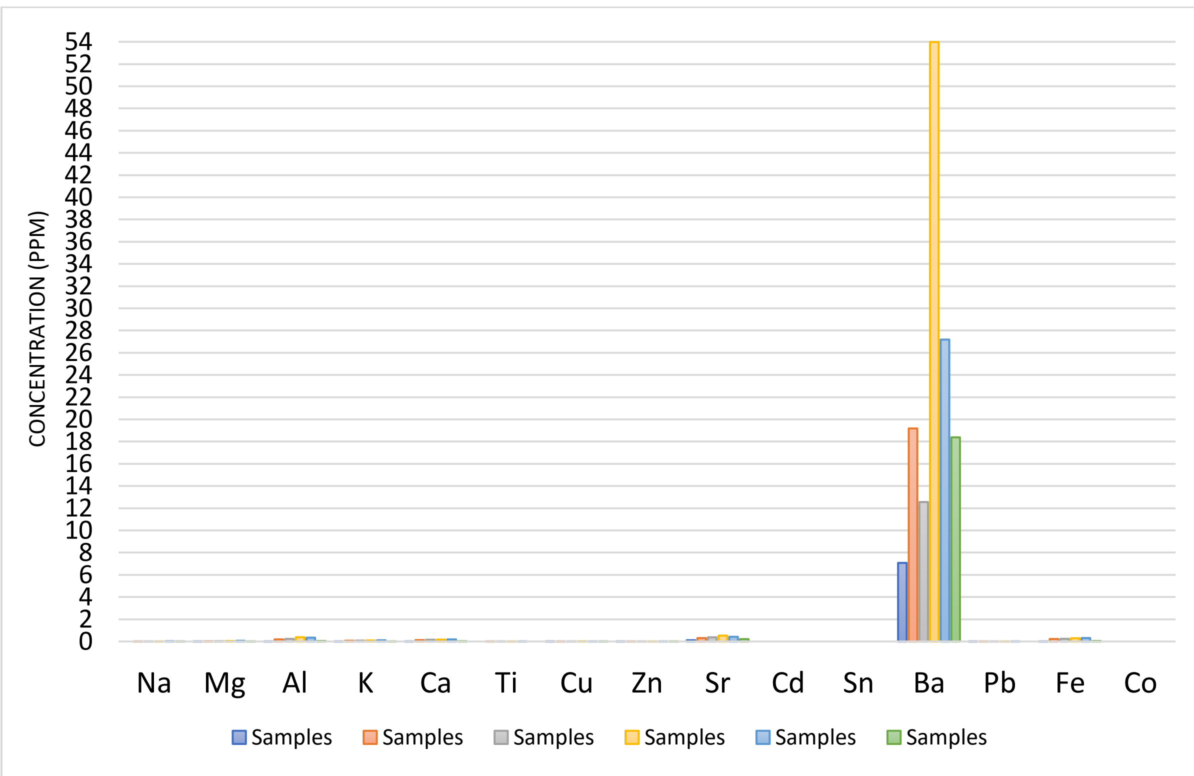


Figure 3.5: Chemical composition of Torkula baryte

3.3.2.1 Alkalinity and Hardness of the Drilling Mud as a Function of Torkula Baryte

Alkalinity and hardness are traceable to the partitioning of CO_2 from the atmosphere, weathering of rock, minerals and soil. The phenolphthalein alkalinity of the drilling fluid formulated based on Torkula baryte and other additives was at 1061 mg/L, as shown in Table 3.5. This quantity of extractable carbonates in Torkula baryte is within the API specification of 3000 mg/kg. Hence, the carbonates in Torkula baryte may alter toxicity when combined with other compounds. On the other hand, the total alkalinity added up to 1658 mg/L, indicating the total amount of calcium hydroxide (lime) required to reduce the pH of the mud to 4.3 from the actual pH value of the drilling mud.

Table 3.5: Soluble Salts of Sulphate, Chlorides and Carbonate

Alkalinity	Remarks
Phenolphthalein Alkalinity	1061mg/L
Total Alkalinity	1658mg/L
Total Hardness as Calcium	**Remarks**
10g Torkula barite	373.3mg/L
70g Torkula barite	143.5mg/L
Chloride and Sulphate Salts	**Remarks**
Chloride Content	1716mg/L
Total Calcium Sulphate	1.6675kg/m^3 (0.575lb/lbbl)

The carbonate alkalinity, chloride count and mineral acidity of Torkula baryte are relatively higher when compared with the American Petroleum Institute (API) Standards, as shown in Table 3.5. This may alter its toxicity and become detrimental to health, except a scavenging element is introduced to reduce the health risk. Most importantly, the high alkalinity of Torkula baryte, on the other hand, may act to resist significant changes in the pH and to control corrosion effectively.

3.3.2.2 Methylene Blue Absorption of Torkula Baryte Mineral

Methylene Blue Absorption (MBA) studies measure the exact quantity of positively charged ion expressed in milliequivalents present in the drilling mud per 100 g of fully dehydrated clay mineral. Table 3.6 and Figure 3.6 examine the reactivity and absorption capacity of Torkula baryte. The volume of methylene blue absorbed at different quantities of Torkula baryte is 14 ml, representing clays base exchange capacity for the drilling fluid. This is because the quantity of aluminosilicate in 10 g and 70 g of baryte gave rise to the same methylene blue capacity. Hence, the MBA and cation exchange capacity (CEC) for 10 g and 70 g baryte is the same (API, 2004, 2009).

Table 3.6: Ionic Character of Clay Minerals

Quantity of Baryte	M. B. C.	M. B. A.	C. E.C. (meq/10g)
10 g	7.0	12.5	0.112
70 g	7.0	12.5	0.112

Figure 3.6: Experimental Result for Methylene Blue Absorption

Baryte and other additives in the drilling mud contributed to 0.012 milliequivalents of reactive clays. This was due to the low dissociation of the baryte minerals. This may limit the performance of shale cuttings on the borehole stability, completion fluid properties, rheology enhancement and other mud properties. However, such observation might also prevent crevice corrosion, rendering Na^+, K^+, Ca^{2+}, Mg^{2+} ion passive due to the inertness of the clay mineral. And so, the material properties of the baryte sample are tailored to suit API specifications for Cl^-, Fe^{2+}, Fe^{3+}(Brevier, J., Herzaft, B. and Mueller, 2002).

3.3.2.3 Mean Metallic Content of Torkula Baryte

The chemical, physical and rheological responses of Torkula baryte depend on the mean values of chemical parameters shown in Figures 3.7(a)-(g) respectively. These were compared with the American Petroleum Institute (API) and the Nigerian Department of Petroleum Resources (DPR) set limits. It was clearly shown in Table 3.7, Figures 3.7 (a), (b) and (d) that lead (Pb) has the highest concentration in Torkula baryte and is followed by calcium and iron minerals. Thus, Torkula baryte contains galena, calcite, hematite, Pyrite, magnetite, sphalerite, brucite, chalcopyrite and chalcocite associated minerals with galena, calcite dominates the host of gangue minerals.

Figures 3.7 (b) to (g) show the exact value of the chemical parameters. Results of the research work of (Ibe et al., 2016) on the reference sample were compared with results obtained in this work. The calcium (Ca), lead (Pb), zinc (Zn), magnesium (Mg), copper (Cu) and cadmium (Cd) minerals in Torkula baryte were within limits set by the American Petroleum Institute (API) and Nigerian Department of Petroleum Resources (DPR). The quantity of iron in Torkula baryte was higher than the API minimum limits; however, lower when compared with the DPR acceptable limit (Ibe et al., 2016).

Table 3.7: Metallic Content of the Barite Samples

S/N	Metals	Concentration (mg/L)/(mg/kg)			API Max. Limit
		Torkula Barite	Ind. accepted Barite	(Ibe et al, 2016)	
1.	Ca	34.0135	415.00	709.00	250
2.	Zn	3.9051	44.60	1.60	140
3.	Mg	8.5726	65.00	64.20	250
4.	Pb	113.8127	193.00	6.00	1000

5.	Cd	0.0008	1.60	1.60	5
6.	Fe	15.6094	400.00	62.20	Zero
7.	Cu	0.3024	1.60	160.00	36

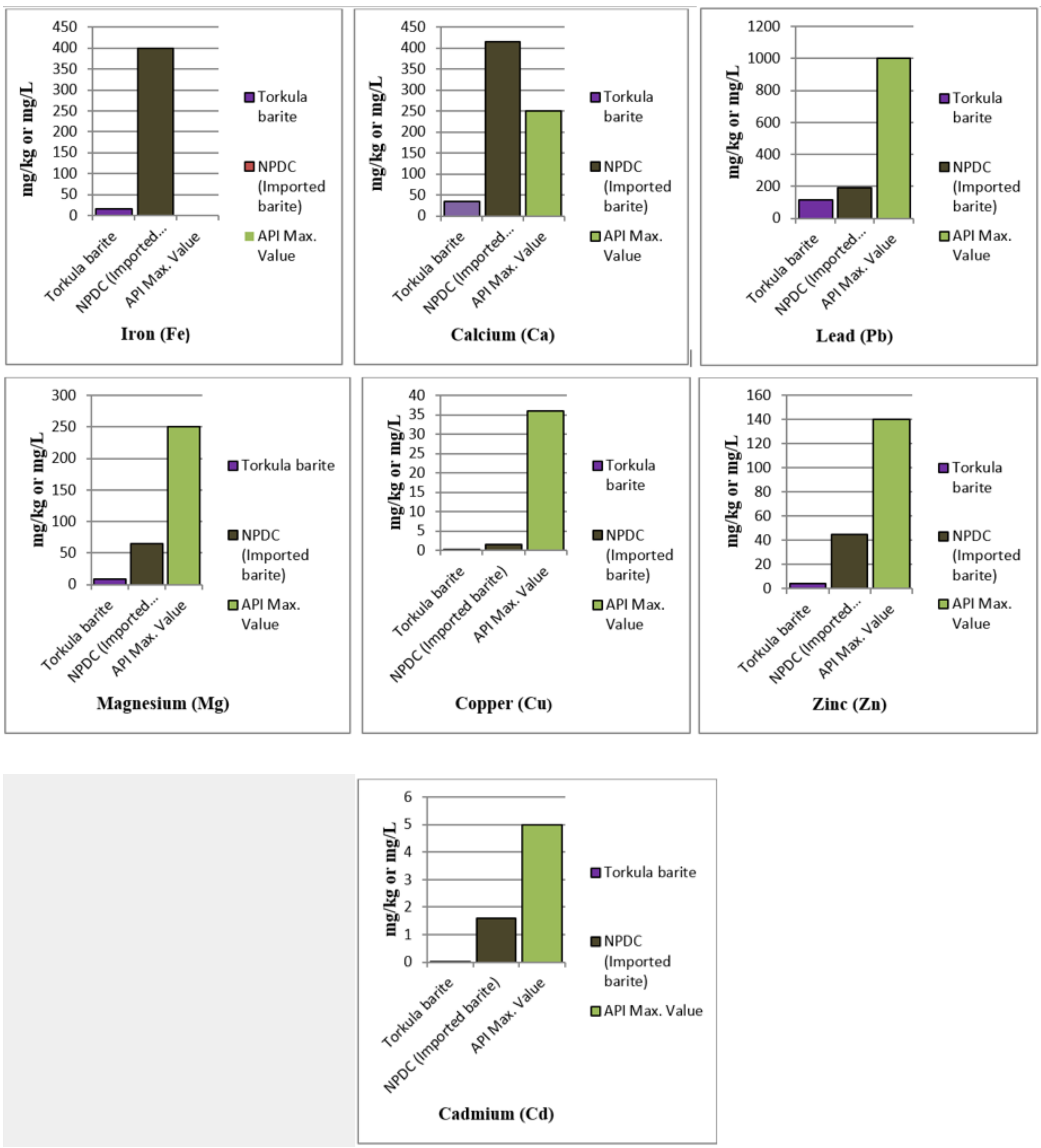


Figure 3.7: Analysis of the Iron Mean values of most dominant Chemical Parameters

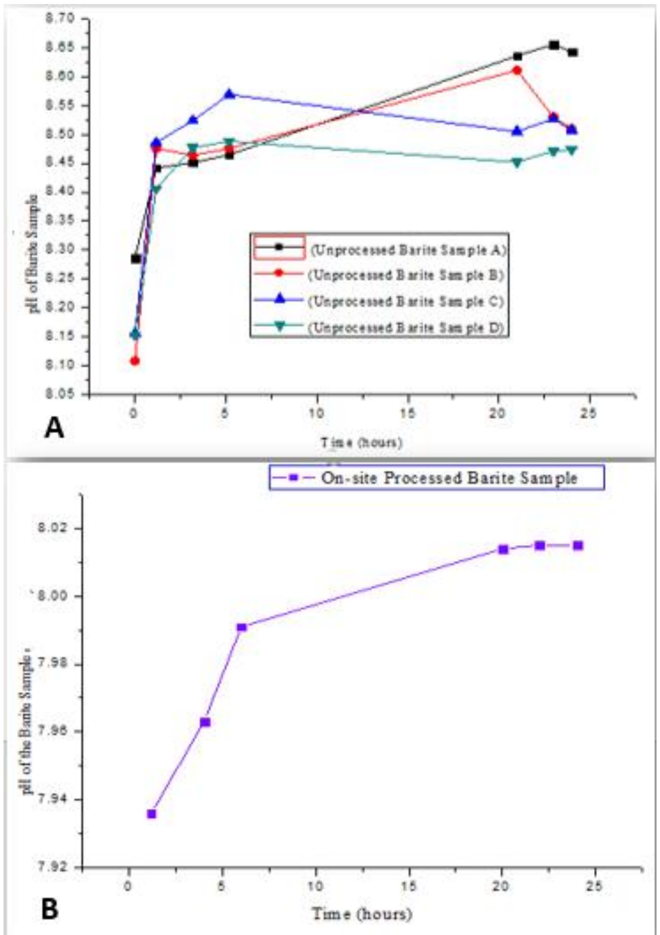
3.3.2.4 Hydrogen Potentials of Torkula Baryte

The Potential of Hydrogen (pH) as a function of electromotive force (e.m.f.) was measured at a given temperature for 24 hours, as shown in Figure 8 (f and g), respectively. The pH of baryte in water was slightly alkaline after the initial 70 minutes, as shown in Figure 8d. However, its alkalinity (hydroxyl ion, OH^-) increased from 7.9 at 28.3 ^oC to 8.0 at 26.3 ^oC after 24 hours. Figure 3.8a clearly explains the rate of hydrogen dissociation of the unprocessed baryte while Figure 3.8b clearly revealed an increase in the hydrogen concentration and baryte (barium and suphate ion) dissociation in water for the on-site processed sample.

The analysed crude baryte samples were slightly alkaline in water, and the status of their alkalinity increased from 8.286 to 8.643, 8.108 to 8.510, 8.156 to 8.507 and 8.153 to 8.474 for samples A, B, C and D, respectively. The pH of baryte samples is above the point of zero charge of pure barite. Thus, the baryte particles could be easily dispersed in fluids to a ensure slight increase in fluid salinity. The pH also favours the dissolution of other drilling mud additives. At moderate fluid salinity, the quality of the filter cake is improved, the mud weight, fluid's gel strength, and fluid loss to the formation become moderate.

Conversely, the hydrogen dissociation of crude baryte was unstable. It increases as the hydrogen ion forms and decreases slightly when it is consumed during the chemical reaction. This clearly indicates the consumption of the hydrogen ion by the activity of associated minerals present in the crude baryte. Despite the shortfall in the pH of the sample, the measured values were within the alkaline range. This was shown in Figure 3.8 (d and f). At these pH values, the solubility of calcium is minimal, and the drilling mud is suitable for the drilling of sandstone formations. This addresses the associated uncertainty and enhances the control measures to erosion and dissolution of freshwater mud. However, the active clays in the mud are easily disintegrated at the high potential of hydrogen to modify materials properties of baryte as a weighting agent in the drilling mud (Ibe et al., 2016).

Its application as a weighting agent in water drilling mud enhances the moderation of hydrogen potentials of the drilling mud within the acceptable limits stated by API. The dissociation of the baryte mineral after 24 hours was minimal when compared with the reference sample and other Nigeria baryte analyzed by (Ibe et al., 2016), (Osokogwu, U., Ajienka, J. A. and Okon, 2014) and (Omoniyi & Mubarak, 2014) as shown in Figure 3.8 (f and g). This shows that the difference in the pH of the Torkula baryte after 24 hours is not as significant, and as such is within the API recommendations of pH=7−≤12.5 (Ibe et al., 2016; Omoniyi & Mubarak, 2014; Osokogwu, U., Ajienka, J. A. and Okon, 2014).. Hence, the pH of the Torkula barite fell within the operational pH regime and standards range of the drilling weighting agent.



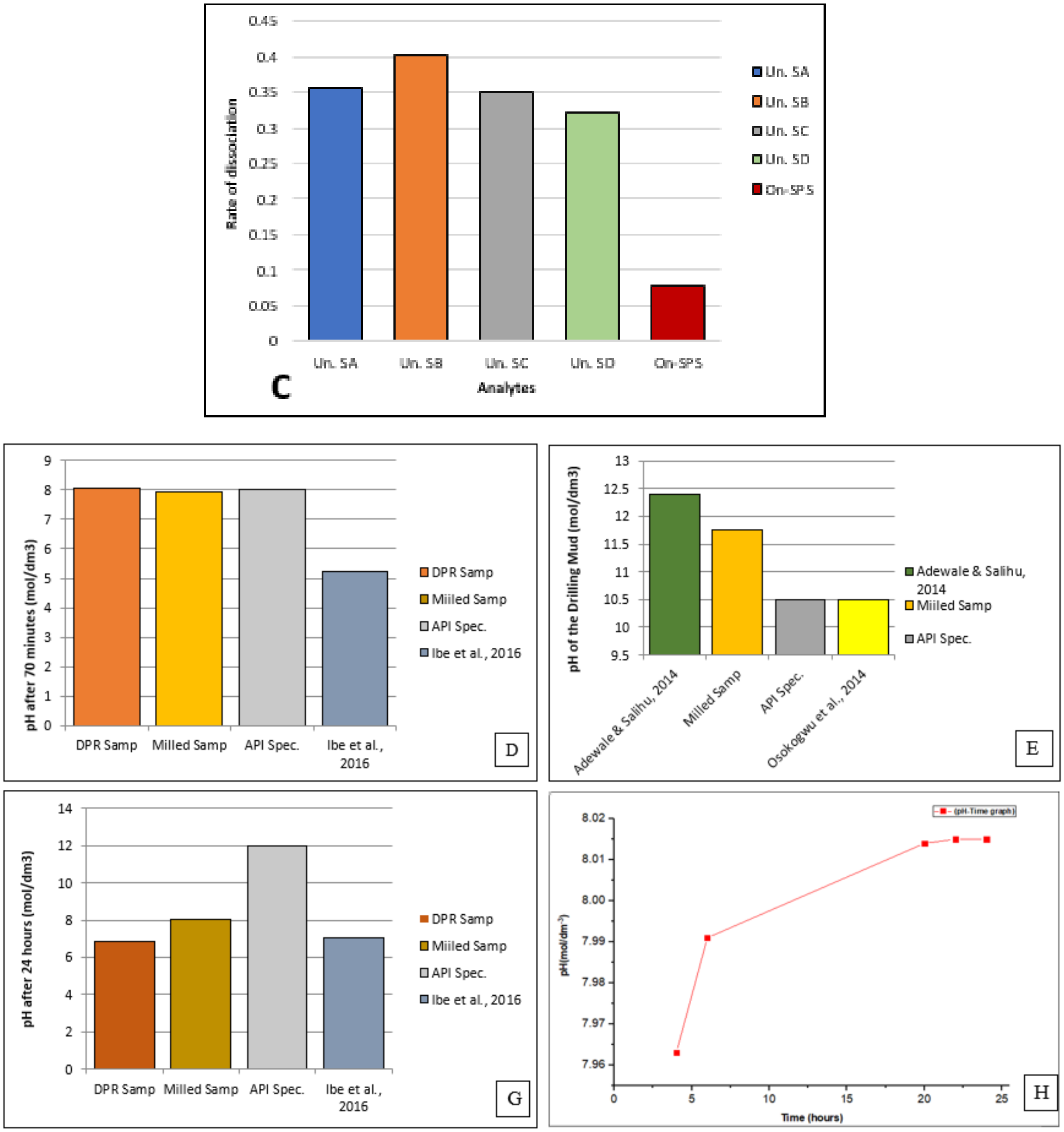


Figure 3.8: (A and B):pH-Time graph for the unprocessed and processed Turkula barite sample from Guma LG A, Benue State, Nigeria, (C): Hydrogen dissociation stability of crude and processed Torkula baryte (Us. SA-Un. SD: unprocessed baryte samples A-D, On. SPS: on-the-site processed baryte), D-G: comparison studies Torkula barite, industrially acceptable grade and baryte deposits reported in the literature.

According to (Christ, 2006), at a pH of less than 9.5, the fatigue life of the drill stem is reduced drastically. Its alkalinity was enhanced by adding sodium hydroxide or lime and raising the pH to 10. In turn, this is said to reduce the corrosion rate and diffusion of oxygen to the surface of metal, thereby increasing its performance in service (Christ, 2006). The extent of alkalinity was slightly reduced from 8.6 in unprocessed baryte sample A to 8.0, as observed with the on-site processed baryte.

Figure 3.8c correctly reveals the pH stability potentials of Torkula barite. The differential hydrogen dissociation of the unprocessed samples was within 0.32 and 0.40 mol/dm^3. However, these reaction products or constants were considerably reduced from 0.40 mol/dm^3 to 0.079 mol/dm^3. At high hydrogen dissociation, the stability of the mud pH became unpredictable. Hence, the on-site beneficiation processes employed has reduced the hydrogen dissociation to enhance the pH stability of the drilling mud.

3.3.3 Physical Properties of Torkula Barite

3.3.3.1 Moisture Content of Torkula Barite

As shown in Figure 3.9, the differential loss in weight of the crude and on-site processed barite were 0.076% and 0.0972%, 0.1225% and 0.1610%, respectively. The average weight of the barite samples decreased from 0.1418% to 0.0866%. Hence, compared to the API standards, the values of moisture content of the barite samples under analysis are below the API maximum value of 1%. However, the on-site processed barite moisture is higher than the crude barite. This increase in the moisture content will affect the mud viscosity negatively and may result in the collapse of the borehole due to varying downhole conditions. Similar experimental observations were documented in work done by (Dhiman, 2012), (Ibrahim, D. S., Amer, N. Sami and Balasubramanian, 2017) and (Osokogwu, U., Ajienka, J. A. and Okon, 2014).

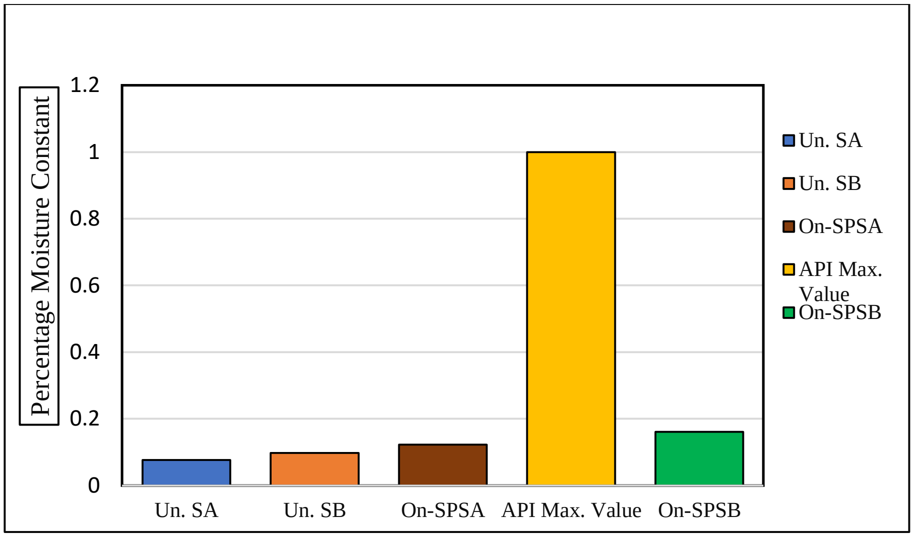


Figure 3.9: Estimation of the weight loss of Torkula baryte samples

3.3.3.2 Specific Gravity of Baryte Samples

The distinctive specific gravity for each barite sample is shown in Figures 3.10 a and 3.10 b. Solid samples C, D, and F, have specific gravities of 3.94, 4.02, and 4.02, respectively. These values are less than the acceptable standards 4.10 SG, specified by the American Petroleum Institute. Samples A and B have specific gravities that are reasonably higher than the globally accepted standards of 4.10 SG but lower than the API 4.21 SG. All the samples have specific gravities that are good for regular drilling operations. These samples have a relatively low quantity of gangue minerals, as revealed in the chemical composition (Figures 3.4 and 3.5 and Table 3.4) and can be further processed to the specific gravity to 4.21. Thus, these baryte rocks or aggregate will add weight to the drilling fluid to ensure a balance of formation pressure during drilling operations.

For the drilling fluid formulation, barite rocks or aggregates are ground or reduced to fine particles (3 µm to 74 µm). Aggregates are mixed and ground as bulk material during the comminution process. The milled samples have specific gravities above or below the require value due to the density of the non-baryte minerals present in the ore. In this study, the specific gravity of the unprocessed barite is 4.02 ± 0.07. The on-site beneficiation process successfully upgraded the specific gravity of milled samples from 4.02 ± 0.07 to 4.15 ± 0.13. The specific gravities of unprocessed or crude baryte, locally processed barite, and other barite deposits reported in the literature were compared, as shown in Figure 3.10 a.

Similarly, the specific gravity of each locally processed baryte was compared to the industrially accepted and global drilling standards for barite as a weighting material. Depending on the local processing methods, certain low-density minerals (impurities in the baryte ore) can be carried away as tailings or trapped in the valuable minerals and reduce the specific gravity of the processed baryte. Such low-density minerals were identified, as shown in Figures 3.4 and 3.7 and Table 3.4. These contaminants in the local baryte can create drilling problems, contribute to water contamination, associated environmental and health risks. Consequently, the mud system should be examined and evaluated to ensure that quality assurance and safety protocols are duly observed for drilling mud additives.

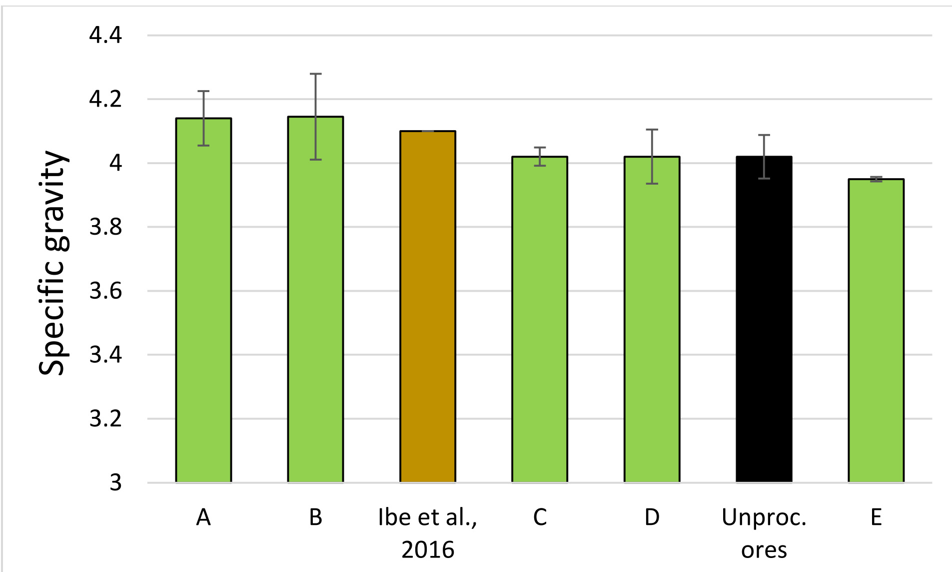


Figure 3.10 a: Comparison Bar Chart for the specific gravities of crude baryte grade, locally processed baryte grade, and other baryte deposits/grade reported in the literature.

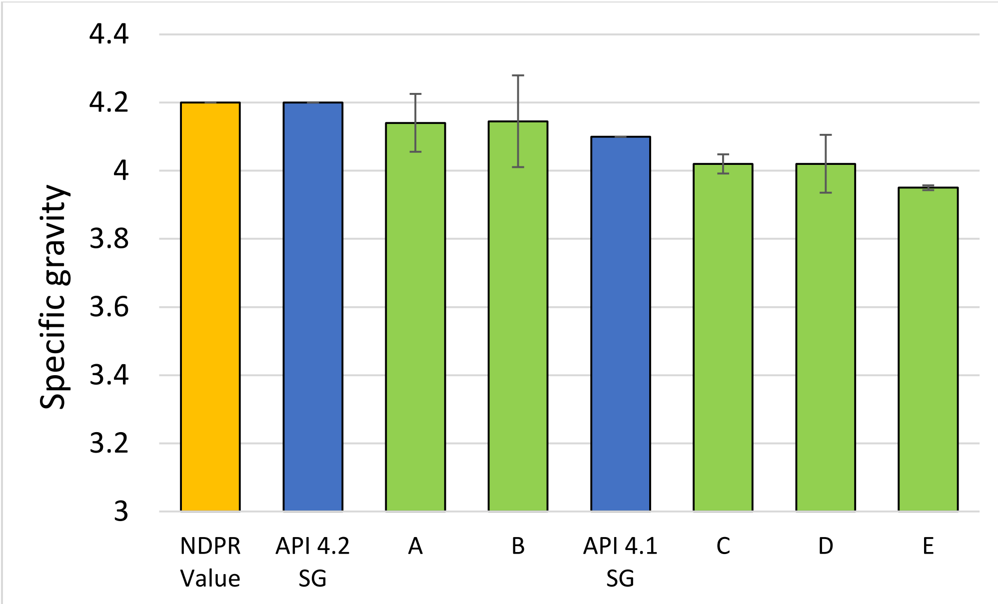


Figure 3.10 b: Comparison Bar Chart for the specific gravities of industrially accepted baryte (Nigerian Department of Petroleum Resources), global drilling standards (API), and locally-processed baryte grades.

3.3.3.3 Hardness of Baryte Samples

The hardness of six baryte samples was measured using the scratch method. Samples A, C and D have a mean value of Mohr's hardness between 3.5 and 4, as shown in Figure 3.11. Also, samples C and D have higher specific gravities and are close to the API SG standard. However, hardness values for samples B, E and F were within 4.5 and 5 Mohr' hardness scale. Differences in the hardness Mohr scale are traceable to the nature of the associated or gangue minerals, as shown by different colours and textures. Weighting agents such as Torkula baryte, having the Mohr's hardness between 3 and 4, can sufficiently protect the drilling bit and preserve the circulation system. Beneficiation of samples A, B, E and F to liberate or extract the gangue minerals from the host will enhance their rheological properties and hardness. However, when such is not addressed before drilling or cementing operation, the wear rate of the bore and the wear debris will be massive.

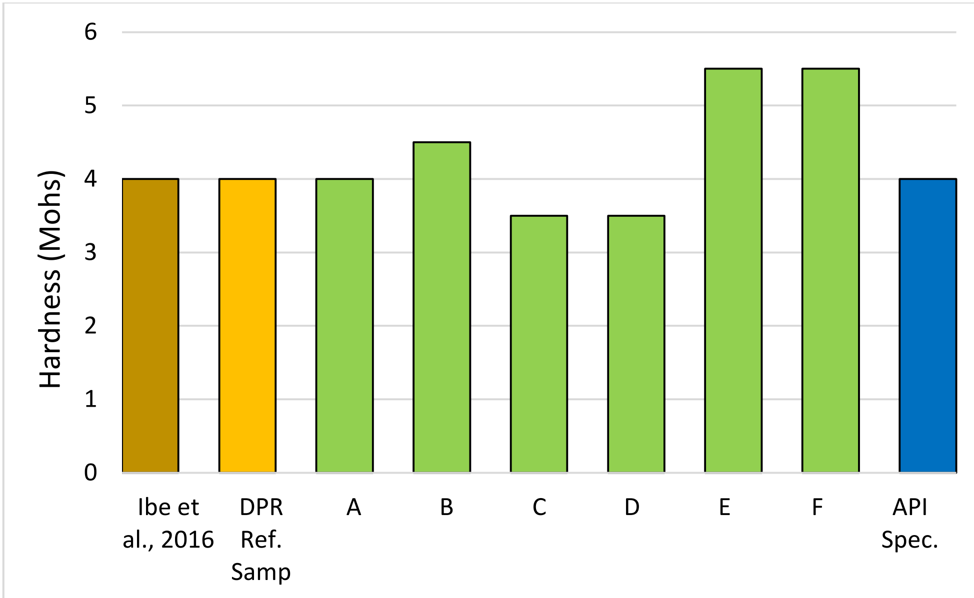


Figure 3.11: Mohr's hardness of the Baryte samples from Torkula baryte field, Benue State, Nigeria

3.3.4 Correlation between the SG and Mohr's Hardness of Torkula Baryte

The qualities of Torkula baryte were evaluated as shown in Figures 3.10(a) & (b) and Figure 3.11 based on their specific gravity and Mohr's hardness. These were validated through thorough comparison with API standards, the reference barite sample commonly used in most of Nigeria's indigenous oil and gas industries and other research works. Four out of seven barite samples from the Torkula barite field in Benue State have SG greater than the API standard. These can be classified as high-grade barite, while two from the remaining three were medium grades. However, sample 2 (coloured barite) belongs to the lower grade class.

Similarly, the wear rate of the bore in drilling operations is mainly traceable to the hardness of the barite mineral. Samples A, C and D were soft, while B, E and F were hard barite minerals. Barite samples B and C were softer than the industrially accepted barite (reference sample) and the two barite samples analysed by (Ibe et al., 2016). These were classified based on the API standards. Conversely, this can be sufficiently corrected by adopting a well-designed washing bay and efficient separation mechanism.

3.3.5 Mud Weight Control Parameter for Torkula Baryte

Mud weight is the exact mass per unit volume of an API drilling mud. It is measured to determine the mud column's hydrostatic pressure required to enhance or control the pore and formation pressures. The significance of the specific gravity of the Torkula baryte was clearly defined in Figures 3.12 (c and e). The addition of the baryte increased the weight of the drilling fluid. Increasing the quantity of Torkula baryte from 5 g to 100 g reflects an increase in the mud weight from 8.49 ppg to 10.5 ppg. Figure 3.12c indicated that industrially acceptable barite increases mud weight from 8.3 ppg to 8.4 ppg.

In contrast, the baryte understudy increased the mud weight from 8.5 ppg to 8.65 ppg, which is up to API standard when baryte addition was increased from 5 g to 10 g. Based on the same drilling fluid formulation, the mud weights of fluids 1, 2, and 3 are higher than the values reported by (Osokogwu, U., Ajienka, J. A. and Okon, 2014), as shown in Table 10 (Osokogwu, U., Ajienka, J. A. and Okon, 2014). The drilling fluids' density formulated based on the use of Torkula baryte has a higher mud weight. Thus, the mud weight is within the acceptable limit and cannot fracture a formation or slow the drilling bits' intermediate rate.

The Torkula Mud Weight test, as shown in Figure 3.12 (e), resulted in the formulation of a mathematical expression to guild the industrial application of the weighting agent. Hence, such graphical analysis will serve as a fundamental control expression for the drilling mud programme. Moreover, this study showed that Torkula barite could be blended with Bentonite to efficienctly increase the drilling mud weight. The Torkula barite as a weighting agent in drilling fluid will sufficiently compete in functions, applications, and performance without excess solids' weight (Bourgoyne, Millheim, Chenevert, 1986; Joel, 2013).

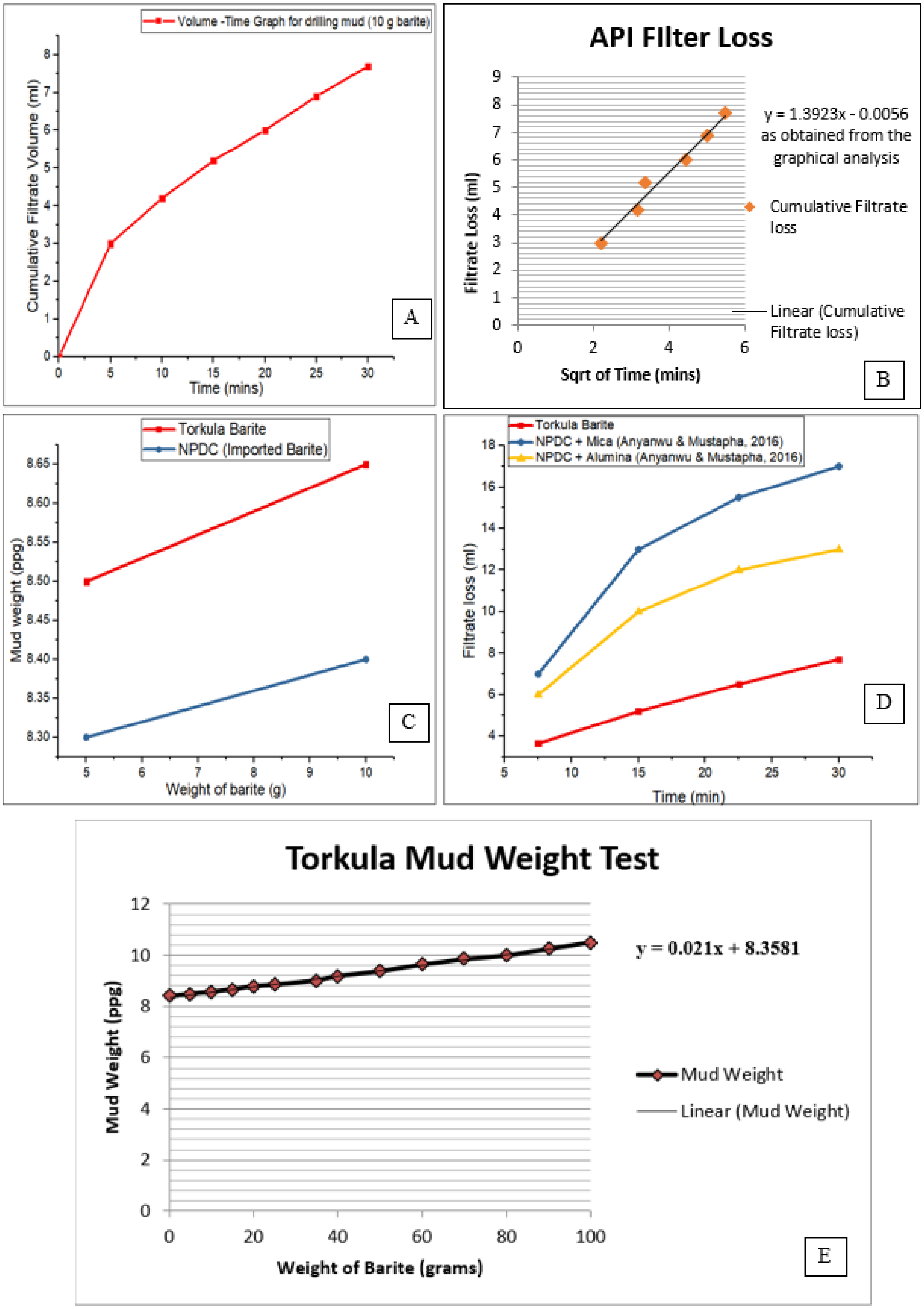
3.3.6 Quality of the Filter Cake as a Function of API Filter Loss

The analysis of the quality of filter cake was shown in Figures 3.12 (a, b and d). It was pronounced that the cumulative filtrate volume increases with time function. However, the volume of filtrate collected at the discrete-time steps decreases gradually with time. This was justified by the quadratic nature of the filtration curve. Similarly, the filtrate volume loss increase with the square of time. The significance of the spurt loss was evident in Figures 3.12

(a) and (b), respectively. The filtrate loss of 3ml was observed as the sporadic rise between 0 and 5 minutes and measured on the API scale to be 0.0056. The negative (minus sign) symbol in the API filter loss expression clearly describes the initial formation processes which gave rise to the filter cake. A thin, firm filter cake was obtained with 10g Torkula baryte, as shown in Table 3.8. Increasing the quantity of Torkula baryte in the drilling mud reduces the spurt loss. However, the thickness of the filter cake was expanded, became firm and flexible. The fluid loss to the filter cake formation increased, and the quality of the cake formed improved. These positive observations are traceable to the drilling fluid's salinity based on the quantity of KCl used in the formulation. Hence, 10 g Torkula baryte enhanced the filter cake quality and reduced fluid loss. Locally processed barite performed better than the industrially acceptable barite, as shown in Figure 3.12 d. This is fundamental to the sealing of the formation pore by the restriction to the influx and further invasion of the fluid

Table 3.8: Analysis of the Filter Cake

Description	Remark	
	10 g Torkula baryte	70 g Torkula baryte
Weight of the filter cake before drying	(1.50 $\pm$0.02) g	19.86 g
The thickness of the Filter cake	1/32 inches	4/32 inches
Quality of the cake	Thin and Firm	Thick, Firm and Flexible



Volume -Time Graph for drilling mud (10 g barite)
Cumulative Filtrate Volume (ml)
Time (mins)
A
API FIlter Loss
y = 1.3923x - 0.0056
as obtained from the
graphical analysis
Cumulative Filtrate
loss
Linear (Cumulative
Filtrate loss)
Filtrate Loss (ml)
Sqrt of Time (mins)
B
Torkula Barite
NPDC (Imported Barite)
Mud weight (ppg)
Weight of barite (g)
C
Torkula Barite
NPDC + Mica (Anyanwu & Mustapha, 2016)
NPDC + Alumina (Anyanwu & Mustapha, 2016)
Filtrate loss (ml)
Time (min)
D
Torkula Mud Weight Test
y = 0.021x + 8.3581
Mud Weight
Linear (Mud Weight)
Mud Weight (ppg)
Weight of Barite (grams)
E

Figure 3.12: Mud weight and filtration properties of the drilling fluids; (A: Rate of fluid/filtrate loss in 30 minutes, B: Linear correlation of the filtrate loss to obtain the API filtrate loss expression, C: Mud weight increase using Torkula barite and industrial accepted barite, D: Comparison of the filtrate/fluid loss reduction potentials of Torkula barite and industrial-grade barite blended with fluid loss control materials (mica and aluminum) as reported in the literature, E: Significance of Torkula barite addition to the mud weight (formulation 2)).

3.3.7 Effect of Addition of Torkula Barite on the Rheology of the Drilling Fluid

3.3.1.1 Plastic Viscosity

The plastic viscosity of the mud varies with the quantity of Torkula barite added as a weighting agent. It increased from 7 cP (0.007 Nsm^{-2}) to 30 cP (0.030 Nsm^{-2}) when the weight of Torkula barite was increased from 5 g to 10 g and reduced to 17.5 cP (0.0175 Nsm^{-2}) as the weight increased from 10 g to 70 g. Such observation revealed that plastic viscosity increases with the amount of solid and might decrease when the solid content is in excess. The increase in plastic viscosity is initiated by a viscous base fluid and excess colloidal solids. The plastic viscosity of drilling fluid with 10 g and 70 g of barite is above the API minimum value and within the range of values reported for the industrially acceptable drilling fluid, as shown in Figure 3.13 and Table 3.10. The low plastic viscosity of the drilling fluid with 70 g indicates that the mud can be used in drilling operations due to the low viscosity of the mud exiting from the bit of the viscometer. The Torkula baryte can be used to increase the plastic viscosity of drilling mud to an acceptable limit. However, such drilling operations will be done at an intermediate rate of penetration (ROP).

3.3.7.2 Apparent Viscosity

Apparent viscosity is measured based on the shear rate at a fixed temperature. The scale is shown as one-half of the dial reading at 600 RPM and specified by the American Petroleum Institute (API) Standards (API, 2009). Its value depends on the shear rate and describes the resistance to the flow when drilling fluid is sheared. The apparent viscosity of the drilling mud increases from 11 lb/100ft^2 to 31.75 lb/100ft^2 when the quantity of Torkula baryte was increased by 5 g as shown in Table 10. The result indicates that the deformation rate of the fluid reduces and its ability to recover from such deformation is higher when the quantity of local baryte in the fluid increases from 5 g to 10 g. However, the plastic viscosity began to experience a slight fall when an additional 60 g of local barite was added into the drilling mud. The higher the resistance to the flow when a fluid is sheared, the greater its ability to remove drill-cutting held due to increased hydrostatic pressure and ensure drilling of new formation. Figure 3.13 also showed that the apparent viscosity reduced from 31.75 lb/100ft^2 to 29.5 lb/100ft^2 as the barite quantity increased from 10 g to 70 g. Such a situation will increase the solid content of the drilling mud. The Torkula barite is compatible with other additives in the drilling fluid. The fluids' apparent viscosities are sufficient to prevent various drilling problems, improve oil well cleaning efficiency, and be suitable for specialized drilling operations within a control volume of liquid and solid content.

3.3.7.3 Yield Point

This is the initial resistance to flow induced by electrochemical forces between the solid content particles constituting a drilling fluid. Such parameter is graphically obtained from the Bingham plastic fluid plot as the zero-shear-rate intercept on the shear stress axis (Abduo, M. I., Dahab, A. S., Abuseda, H., AbdulAziz, A. M. and Elhossieny, 2015). Contrary to the drilling fluid's response in terms of the plastic viscosity, the additional increase in Torkula baryte from 5 g to 10 g reflected a slight fall in the yield point of the drilling fluid. However, the rise in yield point from 3.5lb/100 ft^3 to 24lb/100ft^3 resulted from the additional 60 g baryte added to the mud. This increase and decrease in the yield point indicate the level of the electrochemical forces in the drilling fluid and directly depends on the surface charges of particles in the fluid. As the local baryte quantity increases from 5 g to 10 g, the attractive forces are reduced by a specific chemical reaction between solid particles in the fluid. Figure 3.13 also indicates that the yield point of the drilling fluids (formulation 2) prepared with 5 g, 10 g, and 70 g of local barite were lower than the API minimum requirement. The drilling fluids' ability to suspend and remove solids from the wellbore is low or poor and can be improved. The contribution of Torkula barite as a weighting agent depends on the surface properties, the dynamic conditions, and the volume concentration of the solid components. Increasing the quantity of Torkula barite in a drilling mud will increase the attractive forces and the ability of such non-Newtonian fluid to lift cutting, and clean the wellbore.

3.3.7.4 Gel Strength

This is the shear stress measured at a low shear rate, after which the drilling fluid has set quiescently and is within the period stipulated by API. Such fluid property demonstrates the ability to suspend drill solids during a halt in drilling operations. The emulsion gel structure formed by the drilling fluid composed of 5 g of barite was more stable and increased as the quantity of baryte added into the drilling fluid increased. As the concentration of solids or barite particles in the fluid increases, the attractive forces or extent of the drilling fluid's gelation increases under static conditions. However, high solid or barite concentration may result in flocs formation when the fluid pH is close to the point of zero charges of some solids in the fluid. In such a situation, a low-flat gel curve is produced. Table 3.10 shows that the gel strength of the drilling fluid increased from 2.5 lb/100ft^2 to 3.5 lb/100ft^2 as the baryte quantity increased from 5 g to 70 g. This implies that the addition of Torkula barite into the drilling mud increases gel strength slightly.

Tables 3.9A, 3.9B, and 3.9C indicate that the fluid's viscosity increases as the shear rate decreases. The fluids can form gels in a static situation and flow when the fluid is sheared during flow. Also, the gel strength of fluids is relevant in assessing risk and designing safety protocols that guarantee safe drilling activities. The gel strength values obtained in this study are ideal for ordinary drilling operations but low for specialized functions. In general, during the regular drilling operation, the fluid has sufficient strength to ensure that the mud column's pressure is maintained and kept below the differential pressure between the mud and formation fluids to prevent blowout. However, in specialized operation, the gel strength must be increased to enhance the suspension of cuttings, prevent pipe stuck and hole pack off, and barite sag. This can be done by increasing the quantity of barite dosage or adding a viscosifier to adjust the point of zero charges (PZC) of the fluid. Thus, Torkula barite can produce fluids with flat and thixotropic gels (Abduo, M. I., Dahab, A. S., Abuseda, H., AbdulAziz, A. M. and Elhossieny, 2015; Anyanwu, C. and Mustapha, 2016).

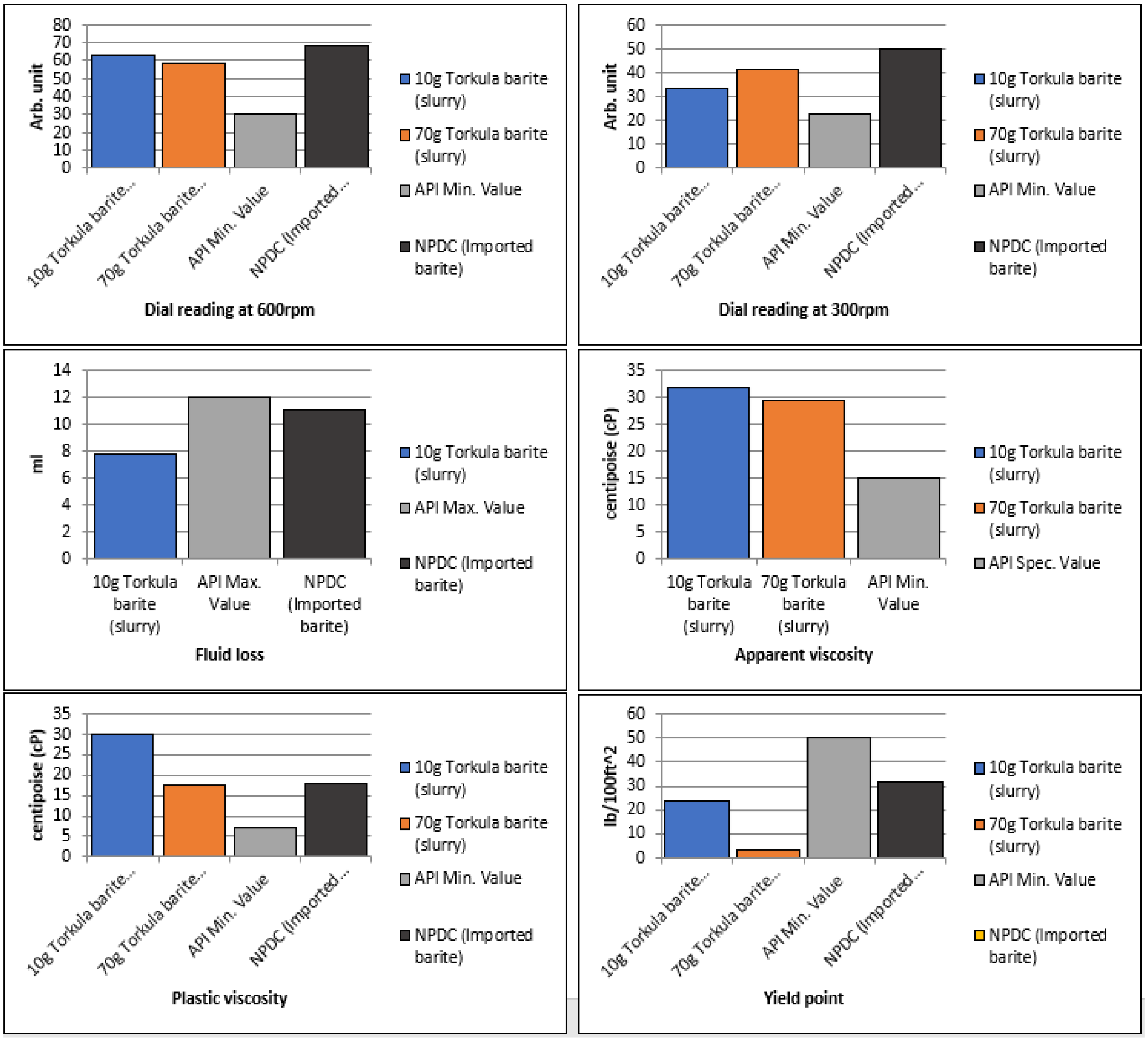


Figure 3.13: Comparison of the Fluid's Composition and Rheological behaviour of Water-Based Drilling Mud using Torkula barite, (Dial reading of rotational viscometer turning the fluids of 10 g and 70 g, at 600 rpm and 300 rpm and fluid properties [fluid loss, apparent and plastic viscosity, and yield point])

Table 3.9A: Shear stress to shear rate behaviour of the Drilling Fluid (5g barite)

S/N	Rotational Speed (RPM)	Shear rate (RPM X 1.703)	Dial Reading (DR)	Shear Stress (DR X 5.11)	Viscosity (cP)
1	600	1021.8	22.0	112.4	0.110
2	300	510.9	15.5	76.7	0.150
3	200	340.6	12.0	61.3	0.180
4	100	170.3	9.0	46.0	0.270

5	60	102.2	7.0	35.8	0.350
6	30	51.1	5.0	25.6	1.500
7	6	10.2	3.5	15.3	1.502

Table 3.9B: Shear stress to shear rate of the Drilling Fluid (10g barite)

S/N	Rotational Speed (RPM)	Shear rate (RPM X 1.703)	Dial Reading (DR)	Shear Stress (DR X 5.11)	Viscosity (cP)
1	600	1021.8	63.5	324.5	0.318
2	300	510.9	33.5	171.2	0.335
3	200	340.6	26.0	132.9	0.390
4	100	170.3	17.5	89.4	0.525
5	60	102.2	13.0	66.4	0.650
6	30	51.1	9.0	46.0	0.900
7	6	10.2	5.5	20.4	2.004

Table 3.9C: Shear stress to shear rate behaviour of the Drilling Fluid (70g barite)

S/N	Rotational Speed (RPM)	Shear rate (RPM X 1.703)	Dial Reading (DR)	Shear Stress (DR X 5.11)	Viscosity (cP)
1	600	1021.8	59.0	301.5	0.295
2	300	510.9	41.5	212.1	0.415
3	200	340.6	33.0	168.6	0.495
4	100	170.3	23.0	117.5	0.690
5	60	102.2	18.0	92.0	0.900
6	30	51.1	13.0	66.4	1.299
7	6	10.2	5.5	28.1	2.755

Table 3.10: Summary of Rheological properties of water-based drilling fluid based on Torkula Barite

S/N	Rheological Properties	Drilling Mud (70g barite)	Drilling Mud (10g barite)	Drilling Mud (5g barite)
1	600 RPM	59.0	63.5	22.0
2	300 RPM	41.5	33.5	15.0
3	200 RPM	33.0	26.0	12.0
4	100 RPM	23.0	17.5	9.0

5	60 RPM	18.0	13.0	7.0
6	30 RPM	13.0	9.0	5.0
7	6 RPM	5.50	4.0	3.0
8	Gel strength @ 10 seconds	3.0	2.5	1.5
9	Gel strength @ 10 minutes	3.5	3.0	2.0
10	Mud weight (ppg)	9.95	8.65	8.5
11.	pH	10.65	11.76	11.97
12.	Plastic Viscosity	17.50	30.00	7.00
13	Yield Point	24.00	3.5	8.0
14	Apparent Viscosity	29.50	31.75	11.00

The addition of baryte to the mud sample impacted the mud's shear stress and viscosity behaviour. Figures 3.14 (a and b) show the shear stress to shear rate relationship and viscosity to shear rate relationship of the mud samples with local baryte as a weighting agent. It was observed that the viscosity of the mud decreases as a function of increasing shear rate. There was a sharp drop in viscosity as the shear rate is increased in the fluid with higher proportion of baryte. Similarly, it was confirmed in Figure 3.14 a that the properties of the fluid changed from a pseudoplastic to plastic fluid as the amount of barite was increased from 5 g to 10 g and then 70 g, respectively. This confirms that the three-dimensional complex structure breaks down due to the applied external force and results in shear thinning behaviour. However, as the quantity of baryte increases, the fluid exhibits yield value and demonstrates shear thinning with increasing shear rate behaviour. The sudden change in the structural characteristics of the fluid due to increased baryte content suggest that the solids in the fluid strengthen the inter-particle or molecular association. However, the structure might still be disrupted, and the position of the particles disturbed at given shear stress.

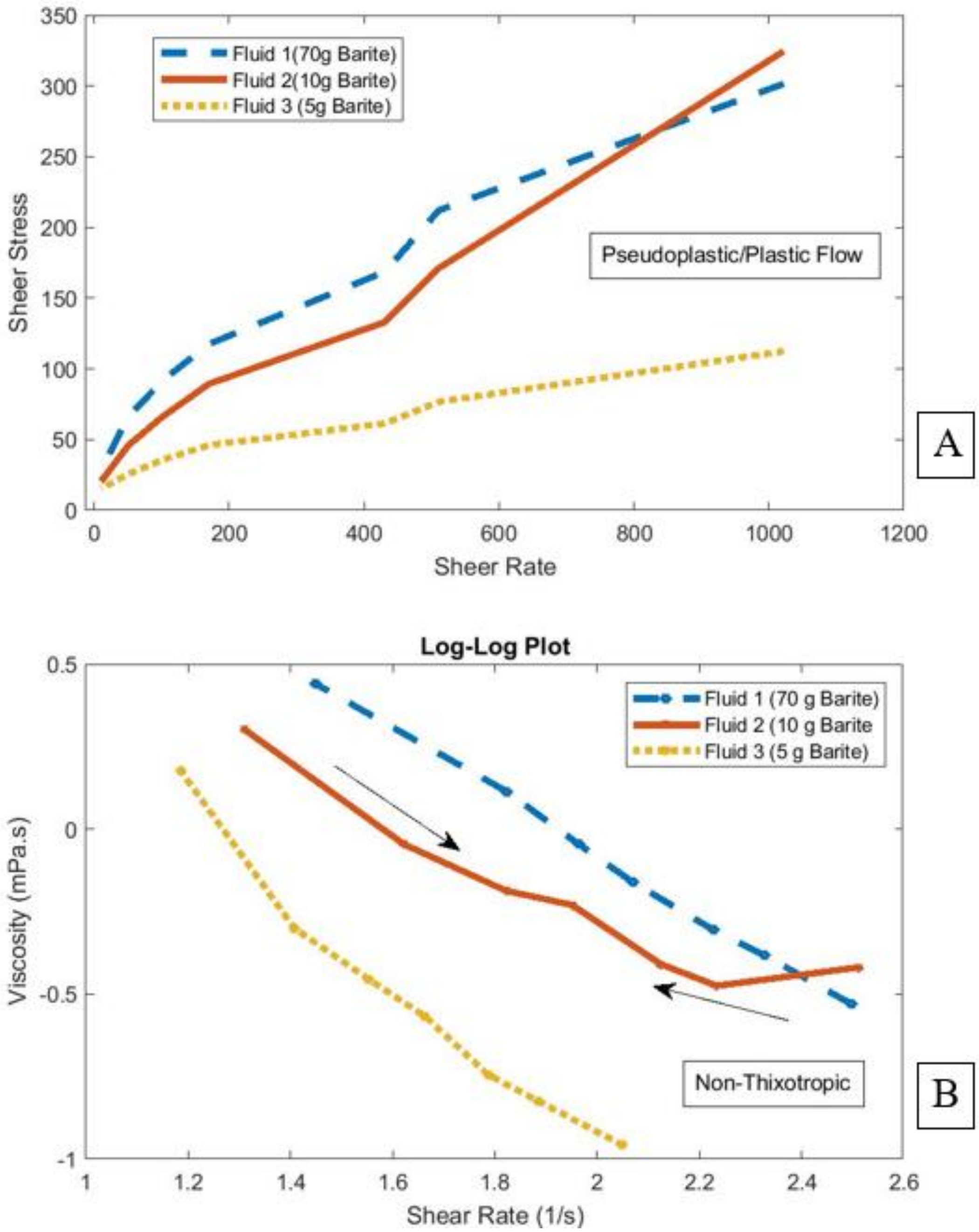


Figure 3.14: Thixotropic properties of fluids formulated using local baryte (A: Shear stress as a function of shear rate, B: Viscosity as a function of shear rate)

Figures 3.14 b and 3.15 clearly show the flow profiles of fluid 1, 2, and 3 respectively. In Figure 3.14 b, the viscosity was observed as a function of shear rate, while viscosity as a function of shear stress is plotted in Figure 3.16. The fluids exhibit the same viscosity at a certain shear rate but behave differently when applied. Similarly, there was a sharp decrease in the viscosities of the fluids on the application of external force due to the breaking of the three-dimensional complex structure and resulting in shear thinning. Also, the viscosity of the fluids was higher at a low shear rate and shear stress, while the viscosity of fluid 2 remained stable as the shear stress is increased beyond 180 mPa. There is an indication that fluid 2 can withstand a higher external force, stain the stable three-dimensional complex structure beyond the application and reconstruction stages. However, fluids 1 and 3 may not retain the complex structure beyond the formulation and production stages. Similarly, it was observed that the decreasing viscosity became steady as the quantity of solid weighting agent is increased from 5 g to 70 g. This confirms a gradual transition from pseudoplastic fluid to plastic fluid as the quantity of solid weighting material increases in the fluid formulation.

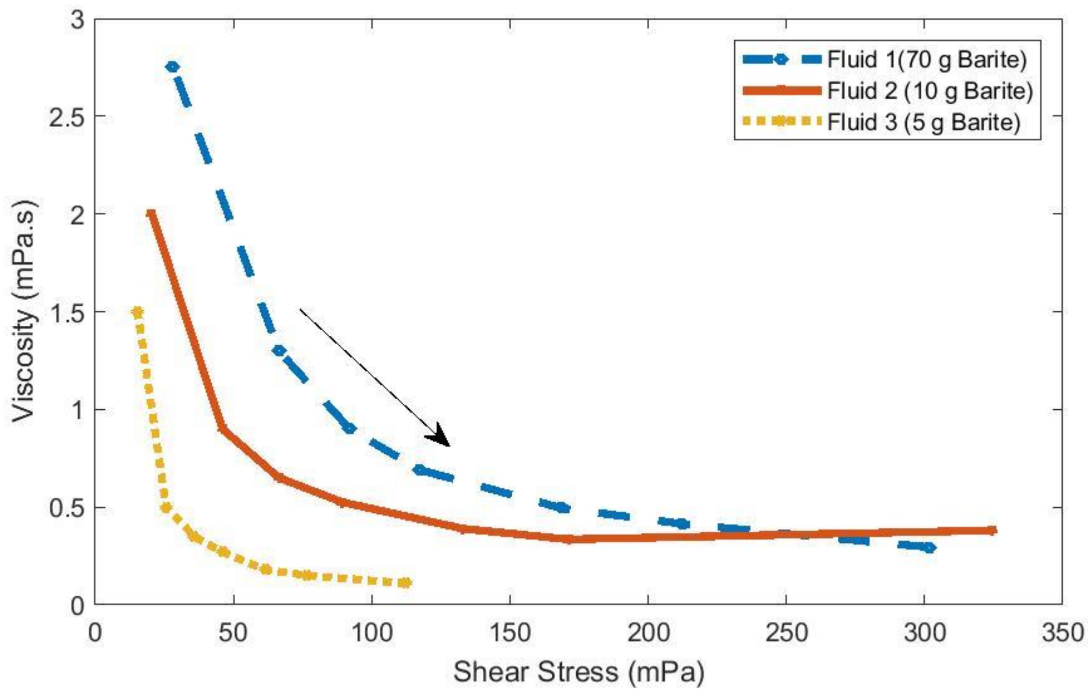


Figure 3.15: Viscosity as a function of shear rate for fluid 1, 2, and 3.

3.3.8 Contributions of Torkula Baryte to the Fluid Properties

Torkula barite water-based drilling mud (WBM) can be described efficiently with behavioural change at different dial readings. Figure 3.14 and Table 3.9 reveal the fluid response of the fluid at different mixing speeds. The figure also shows an increase in the dial reading at 600 revolutions per minute (RPM) and a decrease in the dial reading at 300 RPM when the quantity of baryte is increases from 10 g to 70 g. However, the dial readings at both mixing speeds were higher than the minimum specification recommended by the American Petroleum Institute (API). The information obtained at different speed suggested that the drilling mud belongs to a class of Non-Newtonian fluids. Such reflects a higher viscosity at a low-shear rate (RPM X 1.703) and a lower viscosity at a high-shear rate. From the information in Figure 3.14, the shear stress at each mixing speed, plastic viscosity (PV) and the yield point can be calculated. Hence, Torkula barite can be used to enhance the fluid properties required for both ordinary and specialized drilling operations.

The filtrate or fluid loss from the drilling mud prepared with Torkula baryte is lower when compared with the API specification and other drilling mud formulated using the imported barite. However, it is within acceptable standards. The low value obtained is a function of the amount and particle size of solids (baryte and Bentonite) present in the mud. Hence, the field-scale beneficiation strategies employed on Torkula baryte have greatly improved the quality of the mineral and its acceptance based on the API regulations. The filtrate loss within thirty (30) minutes for Torkula baryte is 7.7 ml as shown in Figure 3.14, while that of the reference sample is 11 ml and the API Specification, which is at 12 ml. This attested that Torkula baryte can sufficiently conserve the liquid content of the drilling mud due to its ability to form a good blend with other additives used in three different formulations (Abduo, M. I., Dahab, A. S., Abuseda, H., AbdulAziz, A. M. and Elhossieny, 2015; Al-Bagoury & Steele, 2012).

The calculated values that correctly describe the internal resistance to the flow of formation fluid into the borehole during the drilling operations are presented in Figure 3.14. This shows the relationship between the fluid flow parameters. The apparent and plastic viscosities of the drilling fluid consisting of Torkula barite are higher than the API minimum values. However, these values were observed to be at the end. This is most appropriate even when there is an unexpected fluid dilution from a water ways.

Similarly, the yield point of the fluid composed of 10g and 70g barite is lower when compared with the API Specification and the value obtained with the imported barite. Furthermore, the yield point observed on the addition of 10g barite is too low, while an average value was obtained when the amount of the weighting agent (Torkula barite) was increased from 10g to 70g. Hence, a higher amount of Torkula barite is required to raise the yield point of the drilling mud. On the other hand, these velocities were measured at different shear rates to determine the rheology model coefficients. They indicated the shear stress as a dial unit or degree at a given shear rate (API, 2004, 2009).

3.4 Conclusion

The pH of the Torkula barite is within the operational pH and the standard range for a weighting agent, as recommended by the American Petroleum Institute. It is appropriate for long-time storage without any operational adverse effect on the drilling mud. Similarly, the moisture content of 0.118% is within the API standards and specification of 1% at maximum. In addition, the differential loss in weight of the crude and on-site processed barite was at 0.076% and 0.0972%, 0.1225% and 0.1610%, respectively. These materials' properties clearly describe the nature and the structure of the barite-water interface, and any observable changes in such material's properties affect the mud viscosity. This is also responsible for the increase in alkalinity and unstable hydrogen dissociation potentials of barite in the drilling mud.

The on-site beneficiation process upgraded the specific gravity of milled samples from 3.82 to 4.13. Barite sample 2 (coloured barite) and unprocessed barite sample A have a specific gravity of 3.85 due to the presence of undesired minerals. These associated minerals are galena, calcite, hematite, Pyrite, magnetite, sphalerite, brucite, chalcopyrite and chalcocite. Six among the seven samples had a little higher SG when compared to the samples analysed by (Ibe et al., 2016). These are below the API standard of 4.2 SG. On-site processed barite has low iron, copper, cadmium, and lead content compared to the imported barite.

The carbonate alkalinity and barite mineral acidity were relatively high compared with the American Petroleum Institute (API) Standards. This may result in some health risk risks and environmental hazards. Better still, the alkaline range of Torkula barite in water can be an advantage in preventing corrosion. However, the effluent from such processes must be treated and ensure that the level of toxic heavy metals such as Zn, Cu, Ba, Cd, Pb, and Fe are within limits recommended by WHO, USEPA, EU and Nigerian Industrial Standard (NIS).

The metallic content such as Ca, Pb, Zn, Mg, Cu and Cd minerals and extractable carbonates in Torkula baryte were within limits set by the American Petroleum Institute (API) and Nigerian Department of Petroleum Resources (DPR). However, the quantity of iron minerals in Torkula baryte is higher than the API set limits but low compared with the DPR set limit. Appropriate tailoring of these properties to suit national and global standards will qualify the use of Torkula baryte mineral in ordinary and specialized drilling operations.

The rheological properties of drilling fluids formulated based on the local barite have been fully described. The plastic and apparent viscosity, yield point, gel strength, mud weight of the fluid, filtration, and thixotropic properties of the fluid are within the API limits. Adding local baryte into the drilling mud improves the rheology and thixotropic properties. This study has identified and expatiated certain relevant information the drilling fluid engineers and other end users need to know in their bid to explore the potentials of the locally processed barite. Practicable recommendations and suggestions are provided in the paper on the necessary adjustments or additional materials required to improve the performance of the weighting agent and mitigate operational impacts in a regular and specialized drilling operation.

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4.0 CHAPTER FOUR: GRAVITY CONCENTRATION OF FINE PARTICLES COMPLEX ORES-CONTAINING BARYTE USING LABORATORY-BUILT MINERAL JIG

4.1 Introduction

Barytes are typically associated with silicates, carbonate, iron oxide, sulphide, and clay minerals (Kecir & Kecir, 2015; Molaei et al., 2018a; Raju, Ratchambigai, et al., 2016). Drilling grade barite is obtained by crushing, grinding, milling, sizing (screening), and beneficiating barite ore deposits (processing and upgrading to remove non-barite minerals). This is to get rid of gangue minerals associated with ores containing barite. Baryte can be liberated from non-barite minerals (gangue phases) in coarse or very fine fractions by gravity concentration, flotation, or leaching to increase the density and quality of the ore (Molaei et al., 2018a; Raju, Ananda, et al., 2016; Wang et al., 2014). Baryte processing in Nigeria and many other developing countries requires environment-friendly, least expensive, easy to use, and efficient methods. Gravity separation is cheap but inefficient for Nigerian baryte processing (Molaei et al., 2018b; Raju, Ananda, et al., 2016). Existing locally fabricated devices used in mining and processing barite ore cannot extract as much of the barite mineral present in the ore. These devices are made of materials that cannot withstand the harsh environment of the mining sites, usually located close to the waterways and under high humid conditions (Odigboh, 2001; Okechukwu et al., 2009). The selection of appropriate/best beneficiation methods depends on the gangue minerals (host rock), the mineral and chemical composition, and grade of the ores containing baryte, mineral degree of liberation, and purity (Gharabaghi et al., 2010; Pattanaik & Venugopal, 2019; Sajid et al., 2021; Singh et al., 2020; Tadesse et al., 2019; Upadhyay et al., 2009).

Baryte processing by jigging and tabling has been reported in the literature (H E Mgbemere et al., 2018; Henry E Mgbemere et al., 2011; Molaei et al., 2018b; Nzeh & Hassan, 2017; Silva et al., 2015). Jigging of baryte is usually carried out on coarse particle sizes to pre-concentrate valuable minerals (-841 + 90 µm) (Henry E Mgbemere et al., 2011; Molaei et al., 2018b; Nzeh &

Hassan, 2017). The jigging process is limited to coarse particles processing and cannot significantly improve the quality of baryte when the particle is liberated in fine size fractions (Bhaskar Raju et al., 2004; Molaei et al., 2018b; Raju, Ananda, et al., 2016; Zhao, Liu, Li, Li, et al., 2014). However, the recovery of baryte and other gangue minerals in ores-containing-baryte is dependent on the degree of liberation. Few pieces of work have shown that ~ 100% of baryte and gangue minerals are free, fully detached, and are no longer interlocked when baryte ore aggregates or rocks are reduced to particle size less than 75 µm (-75 µm #US sieve or -200 #BSS sieve). Similarly, only ~ 91% of baryte and gangue are free or liberated in the ore when the size is reduced to -250 µm (-60 +100 BSS sieve size) (Bhaskar Raju et al., 2004; Molaei et al., 2018b; Raju, Ananda, et al., 2016; Zhao, Liu, Li, Li, et al., 2014). In the case of ore processing by jigging, mineral beds are pulsed, expanded, and loosened off from the bottom of the bed to ensure that fully detached minerals are segregated by the pulsated fluid and recovered.

Baryte is easily liberated from other minerals when ground into fine particles. This explains the failure of jigging to recover barite in baryte ore, improve the quality of baryte concentration, and increase its density. The use of chemical leaching, froth flotation, and hydrostatic pressure for baryte recovery have been recommended and reported on a laboratory scale as the best alternative to jigging (Bhaskar Raju et al., 2004; H E Mgbemere et al., 2018; Molaei et al., 2018a; Raju, Ratchambigai, et al., 2016; Zhao, Liu, Li, LI, et al., 2014). However, these emerging baryte processing methods require materials and resources manufactured on a laboratory scale and are expensive. Using chemicals such as frothers, collectors, depressants, and other industrial chemicals on large-scale barite processing is not sustainable. The cost of cleaning barite products off the chemicals, the surface modification of the minerals, and the consequence of heavy metal contamination of water and soil near the mining sites are currently significant issues of concern. In Nigeria, artisanal and small-scale mining dominate barite mining and processing. These miners cannot afford chemicals other than the usual barite processing method by gravity separation. Jigging and other gravity separation methods are the most sustainable and widely used methods for barite processing in Nigeria (Bhaskar Raju et al., 2004; Jeffery & Hutchison, 1981; Henry E Mgbemere et al., 2011; Raju, Ratchambigai, et al., 2016). However, the quality of jigging products is far below the standards required for most applications. Thus, the need to examine existing barite processing methods by jigging and developing or modifying process conditions (jigging conditions and feed characteristics) to increase the specific gravity of jigging products and achieve high baryte recovery is imminent.

Research has shown that a new jig design exists from old structures, and the latter is a modification of the former. Each of these designs is unique and is used for a particular or general-purpose, as shown in Table 4.1 and Figure 4.1 (Ambrós, 2020; Rao, 2016; Sampaio et al., 2016; Sampaio & Tavares, 2005). Pulsating fluid in a jig may be pulsed by a piston or plunger, diaphragm, and air (Ambrós, 2020; Burt, 1999). Further research by Ambrós (2020) has also shown Denver jig was designed to prevent water leakages through the flanks of the plunger by replacing it with a diaphragm connected to the eccentric shaft to avoid the input of the hutch water and ensure efficient control of the jigging cycle. The subsequent change in the jig design gave rise to other types of jigs as shown in Figure 4.1(Ambrós, 2020; Burt, 1999; Cierpisz, 2017; Sampaio & Tavares, 2005). Thus, the need to modify or optimize existing jig and innovate new jig designs become necessary to keep the techniques competitive, use jigs for the treatment of coarse ores, and as a physical separation method of fine particles complex ores.

Table 4.1: Types of fixed screen jig and their general applications (Ambrós, 2020; Burt, 1999; Sampaio & Tavares, 2005)

Heavy/light products Discharge	Pulsation	Jig Equipment	Common Mechanism Applications
Over the screen/through the screen	Piston	Harz	Coal
	Diaphragm	Jeffrey	Coal
		Bendelari	Ores
	Air-pulsated	Baum	Coal and Ores
		Batac/Tacub	Coal and Ores
Through the screen/over the screen	Diaphragm	Denver	Ores
		Wemco/Remer	Ores
		Yuba	Ores
		Pan-American	Ores
		IHC radial jig	Ores

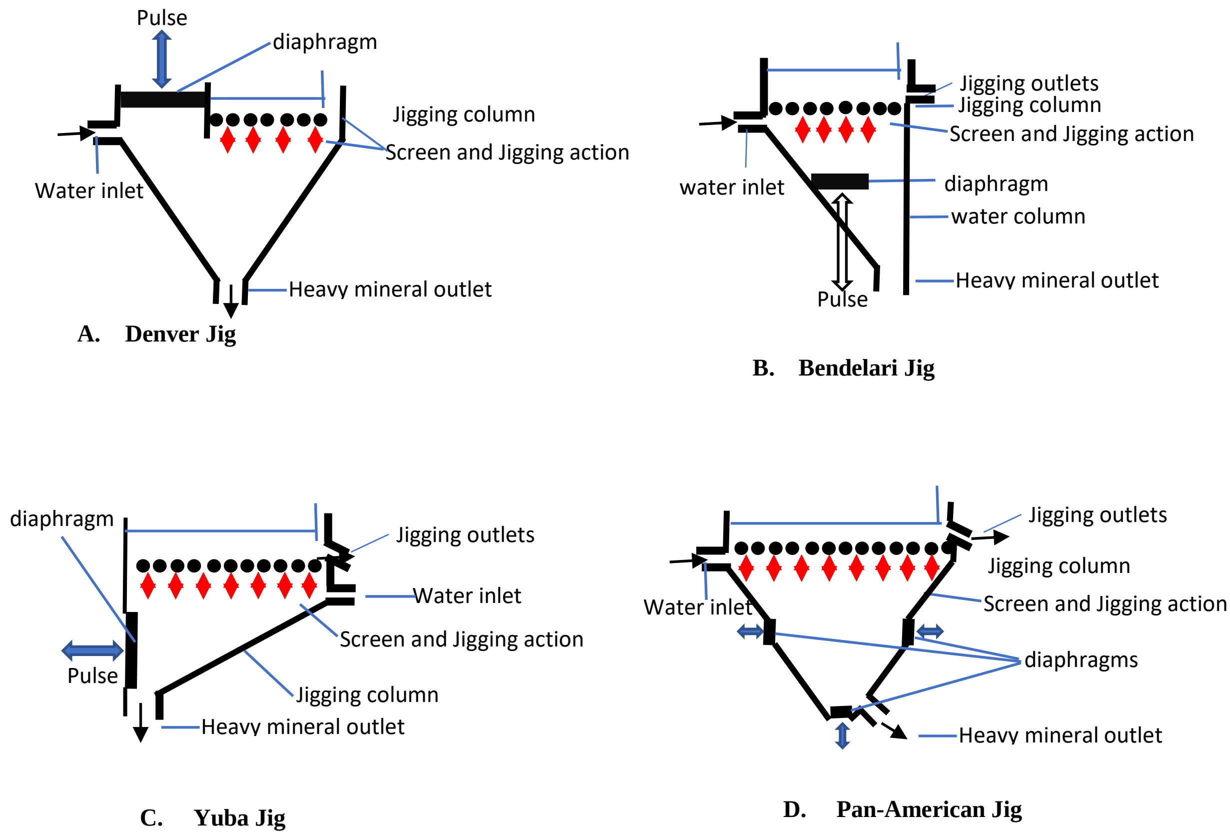


Figure 4.1: Scheme of some diaphragm-type jig (adapted from *(Sampaio et al., 2016; Sampaio & Tavares, 2005)*)

Solids of different densities and sizes segregate and separate. Several conditions favour baryte processing by jigging and ensure an optimized baryte recovery from the ore-containing baryte. These include the jigging conditions (jig amplitude and frequency, water flow rate, mineral bed thickness, jigging, and particles separation time) and feed characteristics (particle size, shape, density, and wettability). Research has shown that feed with a higher proportion of fines has better separation efficiency at relatively low frequency and amplitude (obtained for the size-wise separation efficiency for the optimum jigging condition) (Bhaskar Raju et al., 2004). The fines-dominated feed has less voidage, experience higher drag, and get fluidized at a lower amplitude. This creates a fluidization environment suitable for particle segregation for all size classes, including finer size classes. Others with coarser particles require higher amplitude (more wave energy) for better separation efficiency. Coarse feeds usually have a smaller fraction of fines. Thus, the efficient selection of processing conditions is vital to ensure optimum baryte recovery of the desired and undesired minerals, process yield, particle segregation, mineral degree of liberation, and separation efficiency (Mukherjee & Mishra, 2006; Raju, Ratchambigai, et al., 2016; S. Viduka et al., 2013; S. M. Viduka et al., 2013).

Laboratory-scale mineral processing research involves optimizing jigging conditions and ore characteristics, and the effect of a dependent variable is measured over a range of other independent variables. Such an experiment is carried out using large quantities of research samples, and in most cases, the samples are not available. Therefore, there is a need to fabricate mineral jigs that are small, light-weight with low power consumption, and can be employed to run a series of experiments on a few kilograms of ore samples. In some other applications where few to ten tons of ores are processed, artisanal and small-scale miners need medium-size jigs to extract or recover valuable minerals. This will undoubtedly encourage local ores processing, add value to each solid mineral before exportation, attract end users' collaboration, ensure sustainable utilization and responsible extraction of mineral resources in line with the Sustainable Development Goals (SDGs) 12 and 15 (Afolayan et al., 2021)

This paper presents the use of an entirely fabricated laboratory-built mineral jig (prototype) to process fine particles complex ores containing baryte, iron, lead, and more than five (5) other minerals as impurities in the ores. It demonstrates a mineral jig with fully separated water and jigging columns pulsed by a rubber-end cap diaphragm and driven by a reciprocating device. The paper also discusses the beneficiation of barite ore (barite rocks) of particle sizes -75 µm, -106 µm, -150 µm, and -250 µm using the laboratory-built jig. The particle size was narrowed to examine the effect of degree of liberation of baryte and non-baryte minerals, jig frequency and amplitude on barite recovery and yield, the recovery and rejection of gangue minerals, separation efficiency, and baryte quality (specific gravity).

4.2 Materials and Methods

Baryte rocks were randomly selected from the Kumar barite mining site, crushed and ground by a laboratory jaw crusher and ball mill. The pulverized ore was screened and separated into different particle size range by a mechanical sieve shaker. The ore in each particle size range was processed using the laboratory-built mineral jig at varying jig amplitude and frequency. Schematics for the comminution (crushing and grinding/milling) of baryte rocks are shown in Figure 4.2.

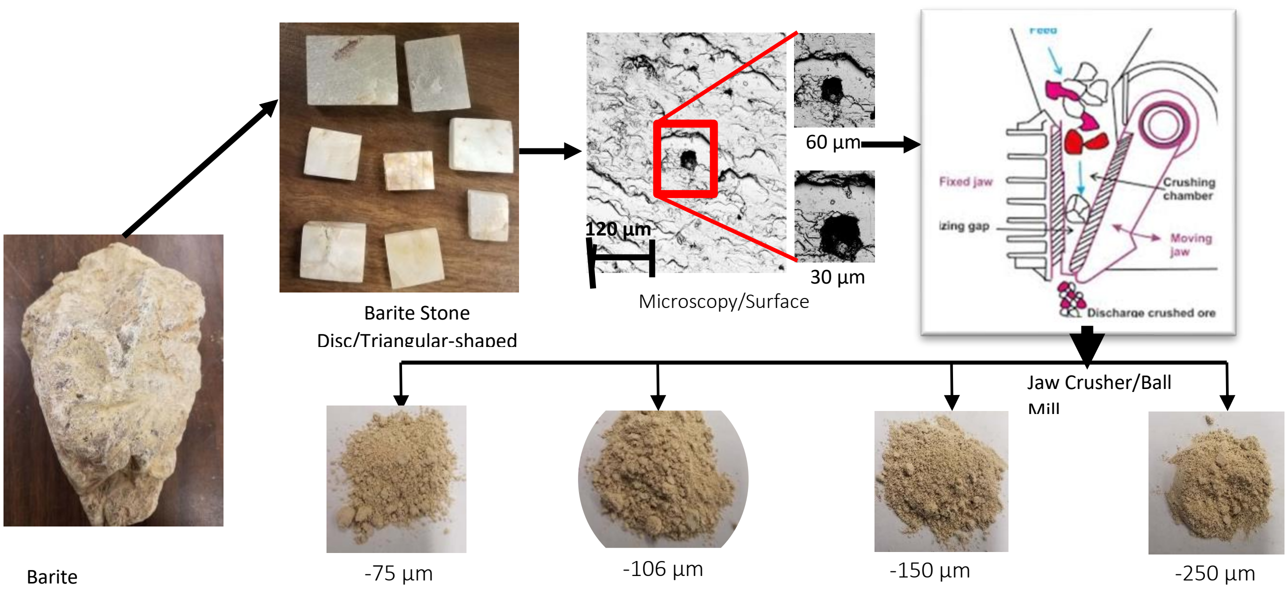


Figure 4.2: Sampling, characterization, crushing, and grinding of baryte rock samples

4.2.1 Experimental Design

A mineral jig with fully separated water and jigging columns was designed using locally available/off-the-shelf materials. Water in the jigging column was pulsed by the rubber-end cap diaphragm and driven by a reciprocating device. The device was manually operated and capable of continuous operation by the rubber-end cap diaphragm and fully controlled jigging conditions. The jigging system was powered by a variable AC power source (VARIAC) to operate the jig at varying frequencies and amplitude. The rubber cap was connected to the reciprocating saw and the waterline connected to the jigging column to examine the jig's operation. Subsequently, the water's displacement up and down in the jigging chamber/mineral bed is shown in Figure 4.3.

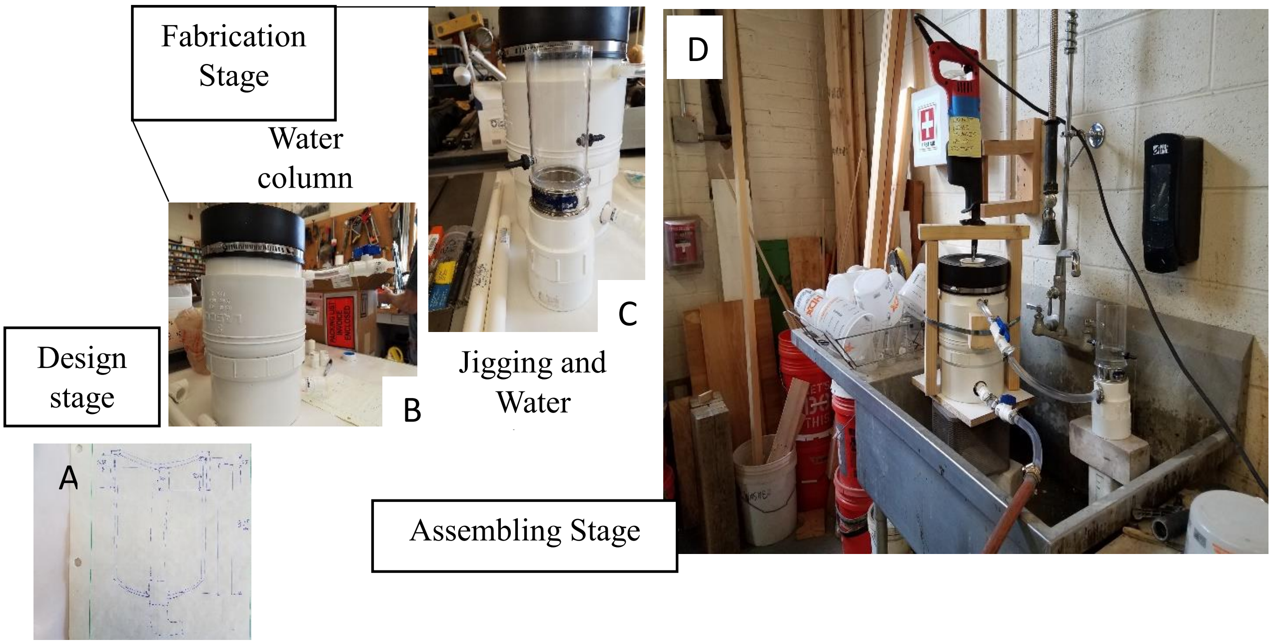


Figure 4.3: Design, fabrication, and arrangement of parts of the laboratory-built mineral jig

Pulverized baryte ore was separated into different size fractions (-75 µm, -106 µm, 150 µm, and 250 µm), as shown in Table 4.2. Within these size fractions, ~ 91% of the baryte and gangue as free or fully detached from each other to ensure particle segregation (Jeffery & Hutchison, 1981). The particle size ranges are selected to narrow the particle size class. This was done to examine the effect of degree of liberation of baryte and non-baryte minerals, jig frequency and amplitude on baryte recovery and yield, the recovery and rejection of gangue minerals, separation efficiency, and baryte quality (specific gravity).

Table 4.2: Selection of particle size fraction (the current study) based on the free fraction of barite and gangue (non-barite minerals) (adapted from (Raju, Ananda, et al., 2016)

Sieve (BSS) Fraction (#)	US Sieve Dimension (microns)	Free barite (%)	Free gangue (%)	Interlocked (%)

-60 to +100	-250	46.36	45.05	8.59
-100 to +150	-150	53.50	44.22	2.48
-150 to +200	-106	57.20	40.50	2.30
-200	-75	~60	~40	< 2.00

4.2.2 Assaying

The recovery and yield of barite, the rejection of impurities (non-baryte minerals), and the separation efficiency of the jigging process are calculated and analysed using equations 4.1-4.4.

Separation efficiency calculated based on the mineral to be separated (alumina)

$Yield\ of\ the\ process$: $Y = \frac{(f-t)}{(c-t)} \times 100\%$ (4.1)

Percentage of alumina in the feed (f), concentrate (c), and tailings (t): impurities.

Rejection of impurities: $R_t^{\ 1} = 100 - Y\frac{c}{f}$ (4.2)

Recovery of alumina: $R_c^{\ 1} = 100 - R_t^{\ 1}$ (4.3)

Recovery of other fractions of the feed: $R_c^{\ 2} = \frac{Y(100-c)}{(100-f)}$ (4.4)

Separation efficiency: $Z = R_c^{\ 2} - R_c^{\ 1}$ Higher separation efficiency, better separation process.

4.2.3 Previous Works

Figure 4.4 presents previous works on jigging and tabling of baryte ores at different process conditions. These studies showed that the specific gravity of baryte ore could be increased by jigging and tabling. However, as reported, the quality of the jigging products, is far below the requirement for oil drilling applications. This shortfall is traceable to several reasons. Jigging is carried out on coarse ores, usually at particles above the liberation size for barite and gangue minerals (non-baryte minerals). Thus, gangue minerals locked in the ore become difficult to separate or liberate from the impurities during jigging. Above the liberation size, the fraction of free baryte and gangue minerals is low and most barytes are still locked in the ores. This was substantiated by (Jeffery & Hutchison, 1981; Raju, Ratchambigai, et al., 2016), as shown in Table 4.3.

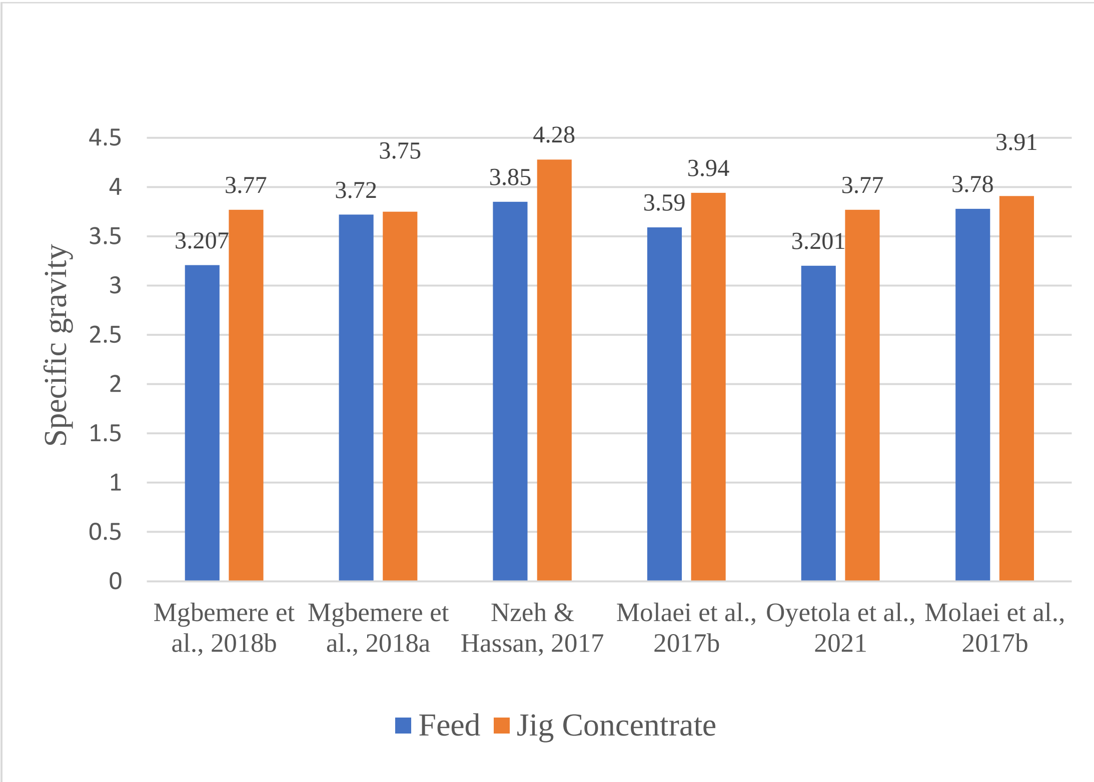


Figure 4.4: Previous works on barite beneficiation by jigging and tabling showing the increase in specific gravities of baryte separated from its ores.

Table 4.3: Liberation of barite mineral at various particle size fractions separated by grinding and screening (Jeffery & Hutchison, 1981; Raju, Ananda, et al., 2016)

Sieve (BSS) Fraction (#)	Free barite (%)	Free gangue (%)	Interlocked (%)
-10 to +14	4.00	10.00	85.00
-14 to +20	7.82	12.29	79.89
-20 to +28	8.05	15.52	76.43
-28 to +35	10.81	38.61	50.58

-35 to +48	16.05	40.30	43.65
-48 to +60	41.93	40.52	17.55
-60 to +100	46.36	45.05	8.59
-100 to +150	53.50	44.22	2.48
-150 to +200	57.20	40.50	2.30
-200	~60	~40	< 2.00

4.3 Results and Discussion

4.3.1 Percentage of Baryte in the Jigging Products

Table 4.4 presents the fraction of baryte within the jigging products. The concentrate or underflow retains ~ 90% to 92% of barite ($BaSO_4$) and ~ 7% to ~ 10% are in the tailings/overflow. Aside from the concentrate and tailings, ≤ 2% of the baryte are lost during jigging. The loss is minimal, and the baryte in the tailing is recoverable using other methods of

	WV: 369 cm^3/min JF: 115 RPM, AMP: 3 cm		WV: 369 cm^3/min JF: 126 RPM, AMP: 2.5 cm		WV: 369 cm^3/min JF: 126 RPM, AMP: 2 cm		WV: 369 cm^3/min JF: 153 RPM, AMP: 1.5 cm	
PS	Tailing	Concentrate	Tailing	Concentrate	Tailing	Concentrate	Tailing	Concentrate
-75 µm	8.50	91.50	7.47	91.06	8.47	90.22	9.99	90.11

concentrating baryte in the jig concentrates.

Table 4.4: Percentage barite in the Jigging Products

-106 µm	8.24	91.76	8.99	90.59	8.40	91.56	7.92	92.08
-150 µm	8.15	91.85	7.03	90.22	7.27	90.85	8.97	90.22
-250 µm	8.50	91.50	7.39	89.55	8.10	89.84	7.77	90.42

WV: water flow rate; JF: Jig frequency, AMP: jig amplitude, PS: Particle Size

4.3.2 Chemical Composition of Jigging Products

Table 4.5 shows a reduction in the quantity of quartz, hematite, and barite increase in all the jigging concentrate. There are ~ 88% $BaSO_4$ in the jig concentrate at the end of a single process in barite jigging. Quartz and hematite in barite ores are reduced from ~ 6.0-6.7% to 4.8-5.94% and from ~ 1.0-1.25 to ~1.1(except when hematite increases from 1.18% to 1.2%). Similarly, the water-soluble salts K, Na, Ca, and Mg fraction are reduced significantly. This shows that some water-soluble salts are in the tailings/overflow at the close of the jigging experiment. Thus, a significant portion of the salts is retained in the jig concentrate. Also, Table 4.5 reveals more $BaSO_4$ in baryte ore of particle size greater than 150 µm. Still, the jigging process increases $BaSO_4$ in jig concentrates (-75 µm, -106 µm, and -150 µm) and exceeds the proportion of baryte in the coarse jig concentrate (-250 µm). It is evident some of the baryte grains and that of the gangue minerals are interlocked, making it difficult to significantly increase the fraction of baryte in the coarse feed (-250 µm).

The jig concentrates possess the excellent chemical composition required by a weighting material for oil drilling mud application. High-density $BaSO_4$ suppresses formation pressure, and the presence of water-soluble salts improves the fluid rheology. The major impurities in the jig concentrate are quartz and hematite. Baryte ore of size fractions -75 µm, 106 µm, and -250 µm retain much quartz. Thus, the quantity of quartz should be reduced and hematite wholly removed from the jig concentrate to improve baryte quality (rheology), increase the specific gravity, and enhance its suitability for oil drilling application.

Table 4.5: Chemical Composition of Jigging Products

WV: 369 cm^3/min; WF: 115 RPM, AMP: 3cm								
	Feed	Concentrate	Feed	Concentrate	Feed	Concentrate	Feed	Concentrate
$BaSO_4$	85.6	87.12	85.61	86.95	85.45	87.76	86.36	87.11
SiO_2	6.06	5.43	6.4	5.34	5.93	5.16	6.69	5.42

Fe_2O_3	1.16	1.14	1.18	1.16	1.25	1.15	1.16	1.13
Water Soluble Salt	7.18	6.31	6.81	6.55	7.37	5.93	5.79	6.344

	Feed	Concentrate	Feed	Concentrate	Feed	Concentrate	Feed	Concentrate
WV: 369 cm^3/min; WF: 126 RPM, AMP: 2.5 cm								
$BaSO_4$	85.6	87.478	85.61	87.782	85.45	87.626	86.36	87.316
SiO_2	6.06	5.94	6.4	5.47	5.93	4.99	6.69	5.51
Fe_2O_3	1.16	1.15	1.18	1.16	1.25	1.15	1.16	1.13
Water Soluble Salt	7.18	5.432	6.81	5.01	7.37	6.384	5.79	6.174

	Feed	Concentrate	Feed	Concentrate	Feed	Concentrate	Feed	Concentrate
WV: 369 cm^3/min; WV: 138 RPM, AMP: 2 cm								
$BaSO_4$	85.6	86.858	85.61	87.516	85.45	87.246	86.36	86.886
SiO_2	6.06	5.384	6.4	4.809	5.93	5.22	6.69	5.655
Fe_2O_3	1.16	1.067	1.18	1.218	1.25	1.098	1.16	1.13
Water Soluble Salt	7.18	6.69	6.81	6.457	7.37	6.436	5.79	6.329

	Feed	Concentrate	Feed	Concentrate	Feed	Concentrate	Feed	Concentrate
WV: 369 cm^3/min; 153 RPM, AMP: 1.5 cm								
$BaSO_4$	85.6	87.998	85.61	87.944	85.45	86.6	86.36	87.104
SiO_2	6.06	4.6179	6.4	5.2143	5.93	5.796	6.69	5.1072
Fe_2O_3	1.16	1.0696	1.18	1.036	1.25	1.0878	1.16	1.071
Water Soluble Salt	7.18	6.315	6.81	5.81	7.37	6.516	5.79	6.718

Water-soluble salts are Ca, K, Ma, Na, and moisture content of ≤1.5%

4.3.2 Baryte Yield by Jigging Barite Ore

Figure 4.5 shows the yield of baryte from barite ore during the jigging process. Baryte ore of particle size less than 250 µm has the highest baryte yield. This agrees with previous studies that coarse ores have better mineral yield. As jig frequency increases, the baryte yield of the jigging process varies across particle size fractions. Jig frequency of 115 RPM gave the best yield of baryte for particle size less than 106 µm while the highest baryte yield of particle size fractions -

75 µm and -150 µm is at 126 RPM. The coarse feed has good mineral yield at high and low jig frequency and amplitude. However, an optimum jig condition is required to increase barite yield for particles less than 150 µm. Optimum barite yield is attainable for large particle sizes at higher jig frequency (153 RPM) and lower jig amplitude (1.5 cm).

In contrast, higher amplitude (2.5 cm-3 cm) and lower frequency (115 RPM-126 RPM) are preferred for small-size baryte concentrate. This agrees with conclusions from previous research (Bhaskar Raju et al., 2004; Mukherjee & Mishra, 2006). Thus, baryte yield by jigging is size-dependent and is improved by optimizing jigging conditions.

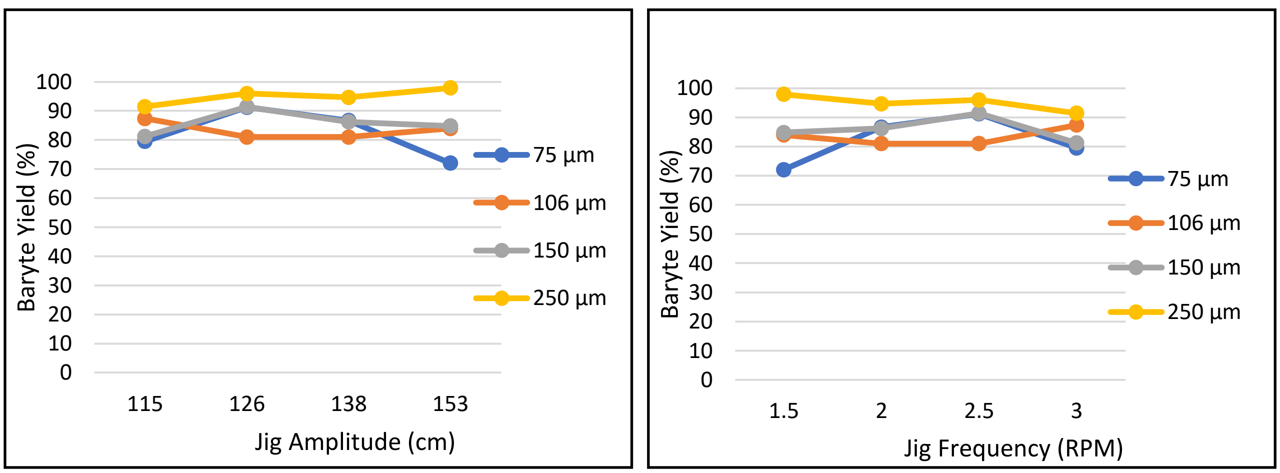


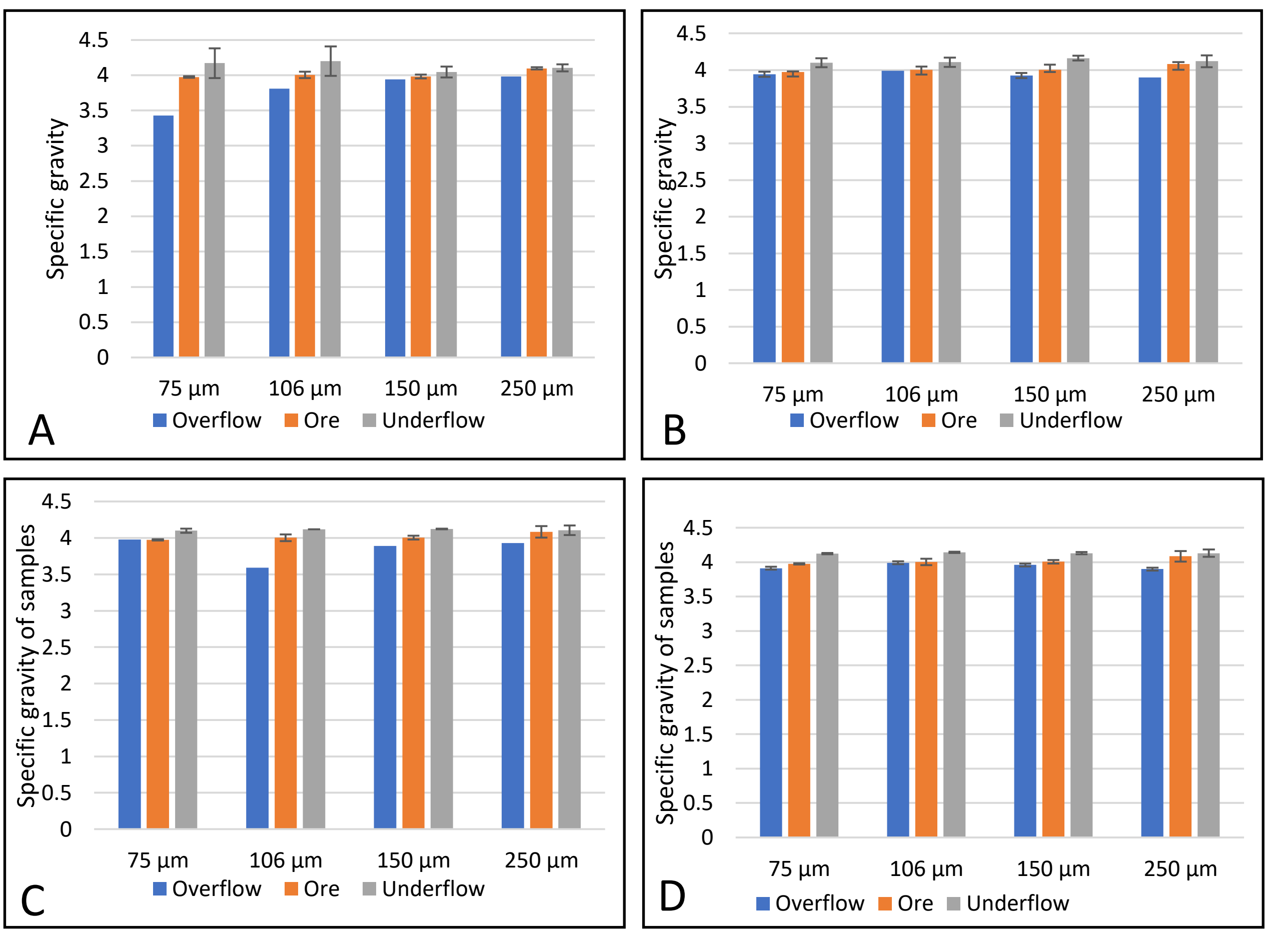
Figure 4.5: Baryte yield at different jigging conditions and particle size (a): varying jig amplitude; (b): variable jig frequency.

4.3.2 Specific Gravity of Jigging Products

Figure 4.6 presents the specific gravities of jig tailings, feeds, and concentrate at different jigging conditions. The effect of jig frequency and amplitude on baryte ore processing are examined, and optimum jigging conditions for increasing the density of jig concentrate are attained. Water-flow rate of 369 cm^3/min, jig frequency of 115 RPM, and jig amplitude of 3 cm contribute to the increase in specific gravities of barite ore of particle size less than 75 µm and 106 µm. The specific gravities increase from 3.97 to 4.17 and 4.00 to 4.20 for size fractions. However, there was no significant increase in the specific gravities of ores of particle sizes greater than 106 µm (-150 µm and -250 µm) under the same jigging condition. The percentage improvement of the jigging process, based on the specific gravity, increases from 0.98 (-250 µm) to 4% (-150 µm) and 5% for finer jig concentrate (-75 µm and 106 µm). Thus, the recovery of quality baryte from its ores depends on the feed characteristics, jig amplitude, and frequency. This agrees with previous works on gravity separation.

Above jig frequency of 115 RPM, the specific gravities of baryte ores in larger size fractions improve. At a jig frequency of 126 RPM, the specific gravities increases from 4.00 to 4.16 for ore of particle size less than 150 µm. Likewise, the specific gravity of ores (-250 µm) increases from 4.08 to 4.12. The percentage improvement for coarse jig concentrate (-250 µm) is from 0.98 at 115 RPM to 3.25 at 153 RPM, respectively. However, there was no significant increase in the specific gravities of smaller-size jig concentrates (-75 µm and -106 µm) at higher jig frequency (138 RPM and 153 RPM) as compared to the improvement observed at 115 RPM and high jig amplitude (2.5 cm-3 cm). Although the further increase in jig frequency increases the specific gravity of the coarse ore (-250 µm), such an improvement is not significant, and the values are far below the API requirement for a weighting agent in oil drilling mud. The specific gravities of the tailings/overflow are still high, very close to that of the feed in all cases. This indicates that heavy fines also result in the tailing alongside light fines, thus increasing the specific gravities.

The optimum jigging condition to increase the specific gravities of jig concentrate is both size and density-dependent. Baryte ores with a high volume of fine particles retain the dense materials and experience an increase in density at low jig frequency (115 RPM) and high jig amplitude (3 cm). As the jig frequency is increased beyond 115 RPM, the specific gravity of coarse jig feed of size less than 150 µm increases. However, the specific gravities of coarse jig concentrate of particle size greater than 150 µm do not increase significantly despite low-density tailings recovered from the ore fraction. This is due to high proportion of quartz. Previous results and discussion on the chemical composition of jig products (Table 4.4) also confirm that despite high baryte yield in coarse jig concentrate, it does not translate into a significant increase in specific gravities.



A
Specific gravity
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
75 µm
106 µm
150 µm
250 µm
Overflow
Ore
Underflow
B
Specific gravity
C
Specific gravity of samples
D
Specific gravity of samples

Figure 4.6: Specific gravities of jigging products (tailings and concentrates) and feeds at different jigging conditions and particle sizes (A): Water flow rate [369 cm^3/min], Jigging frequency [115 RPM], and Jig amplitude [3 cm]; (B): Water flow rate [369 cm^3/min], Jigging frequency [126 RPM], and Jig amplitude [2.5 cm]; (C): Water flow rate [369 cm^3/min], Jigging frequency [138 RPM], and Jig amplitude [2 cm]; (D): Water flow rate [369 cm^3/min], Jigging frequency [153 RPM], and Jig amplitude [1.5 cm]

4.3.3 Recovery of Baryte and Rejection of Non-barite Minerals

Figure 4.7 presents the weight or quantity of baryte recovered and tailings (undesired minerals) retained in the jig concentrate. It quantifies fractions of baryte that can be recovered from total liberated/free barite or undesired mineral to be withdrawn from the jig concentrate. This is simply the assaying of the ore and describes the grade of the ore. Baryte recovery from the ore is ≥ 74% for all size fractions. The quantity of baryte recovered from the ore varies and is affected by jigging conditions. Baryte ore of particle size greater than 150 µm (-250 µm) has the highest baryte recovery (value mineral). The rate of recovery increases from ~ 90% to ~ 99% for coarse jig concentrate (-250 µm) as the jig frequency increases from 115 RPM to 153 RPM. Likewise, high baryte recovery is observed for smaller fractions (-75 µm, -106 µm, and -150 µm). The recovery rate of baryte in ore of particle size less than 75 µm and 150 µm increases from 79% to ~ 94% at jig frequency of 126 RPM while baryte recovery drops from 86% to 83% for particles of sizes less than 106 µm. Although the recovery of coarse ore deposits is high, the rejection of impurities is low, and more of the undesired minerals are retained within the jig concentrate. This indicates that complex particles containing one or more gangue minerals associated with the value minerals exist in the slurry and affect the sharpness of mineral separation during jigging.

Beyond the optimum jigging condition, the recovery dropped for all materials of different particle sizes. Likewise, the number of impurities (undesired minerals) retained in the jig concentrate increases. The recovery for fines (-75 µm, -106 µm, and -150 µm) is high, and the undesired minerals are less retained in the jig concentrate than the coarse jig concentrate. It is important to note that baryte recovery or yield is affected by the liberation size of the valuable mineral, the quantity of middling (i.e., composite particles containing barite still locked with one or more non-barite minerals), and jigging conditions. Thus, the recovery of value minerals is improved at optimum jigging conditions for each particle size range.

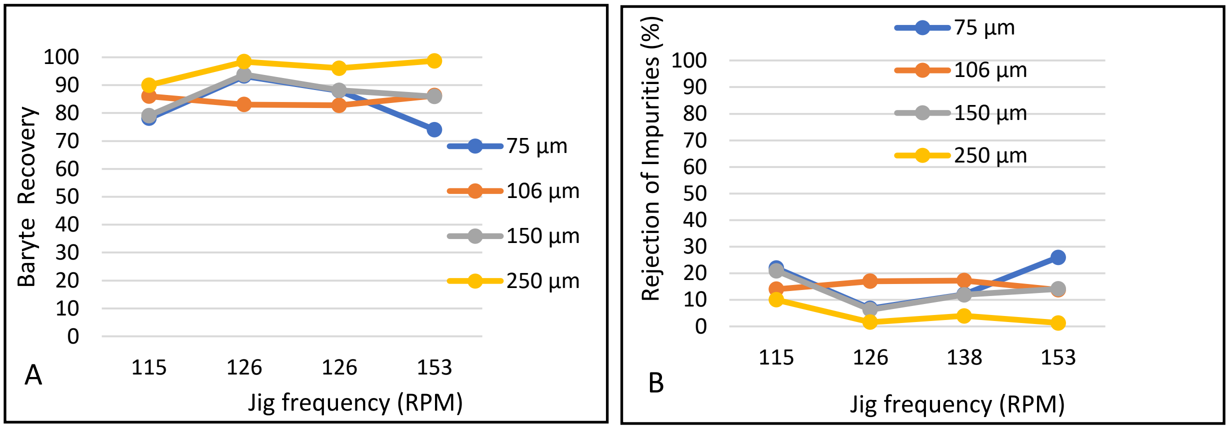


Figure 4.7: Rate of baryte recovery and rejection of other non-baryte minerals in the feed (A): percentage recovery of barite during jigging, and (B): removal of non-barite minerals and other light-weight minerals from the ore.

4.3.4 Separation Efficiency of the Jigging Products

Figure 4.8 shows the separation efficiency of barite (value mineral) and non-baryte minerals in the ore across particle size ranges. Jig feeds of particles greater than 150 µm (-250 µm) have the least separation efficiency at the lowest jig amplitude and highest jig frequency. The separation efficiency increases as jig amplitude increases and a sharp increase in separation efficiency are observed for jig concentrate of particle sizes less than 150 µm (-75 µm, 106 µm, and -150 µm). Likewise, optimum conditions for all size fractions are attained at a jig amplitude of 2.5 cm and a jig frequency of 126 RPM. This implies that better separation was achieved whenever the ore particle was pulsed and raised to a significant height to allow differential settling of particles based on their sizes and densities.

The calculated value for baryte recovery and other minerals is close in this study. Despite high mineral liberation for particle size less than 150 µm, the separation efficiency cannot be raised beyond 16% at optimum jigging conditions (126 RPM, 2.5 cm). This explains the consequence of a strong association between the value mineral and the undesired minerals which gave rise to middling within the slurry and reduced the sharpness of mineral separation.

As the separation efficiency of the ore (-150 µm) reaches the optimum, an increase in the specific gravity of the jig concentrate is observed. The high specific gravity achieved at 115 RPM and 3 cm (Figure 4.6) is traceable to the separation efficiency, the fraction of free minerals, and jigging condition. Also, optimum baryte separation depends on the fraction of baryte and gangue minerals that are free or fully liberated by grinding and screening baryte ore into different particle sizes.

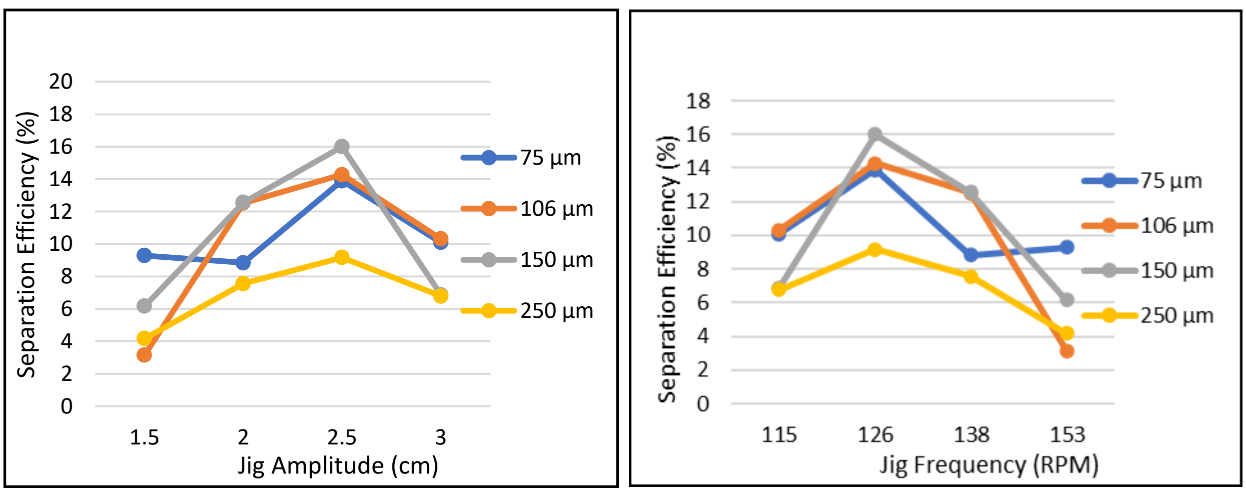


Figure 4.8: Separation efficiency of baryte at different jigging conditions (water flow rate, jig frequency, and amplitude (a): efficiency of baryte separation as jig amplitude increases, and (b): as jig amplitude increases.

4.3.5 Optimum Jigging Conditions to Increase Specific Gravities of Jig Concentrates

Figure 4.9 presents the specific gravities of the jig concentrates of different particle sizes pulsed under varying jigging conditions. The best specific gravities (4.17 and 4.20) for fine baryte ores (-75 µm and -106 µm) are obtained at the jig frequency of 115 RPM and jig amplitude of 3 cm. However, coarse jig concentrates (-150 µm and -250 µm) have lower specific gravities (4.10 and

4.05) at low jig frequency (115 RPM). As the jig frequency increases and jig amplitude falls, the specific gravities of coarse feed increase and the fines fall. At jig frequency of 126 RPM and 158 RPM, optimum specific gravities of 4.16 and 4.14 were achieved for coarse jig concentrates of particle size less than 150 µm and 250 µm, respectively. This implies that the small particle size ore requires lower jig frequency (fewer cycles) and maximum displacement of solids to allow differential settling of solid under gravity. This agrees with conclusions from previous works on baryte jigging (H E Mgbemere et al., 2018; Henry E Mgbemere et al., 2011; Molaei et al., 2018a; Nzeh & Hassan, 2017; Raju, Ratchambigai, et al., 2016). Increasing jig frequency at jig amplitude of 2.5 cm help improves the specific gravities (SGs) of the coarse jig concentrates (-150 µm and -250 µm). However, the quality of value mineral (specific gravity) in -250 µm size fraction cannot be increased beyond 4.13, which is far below the requirement of a weighting agent in oil drilling mud.

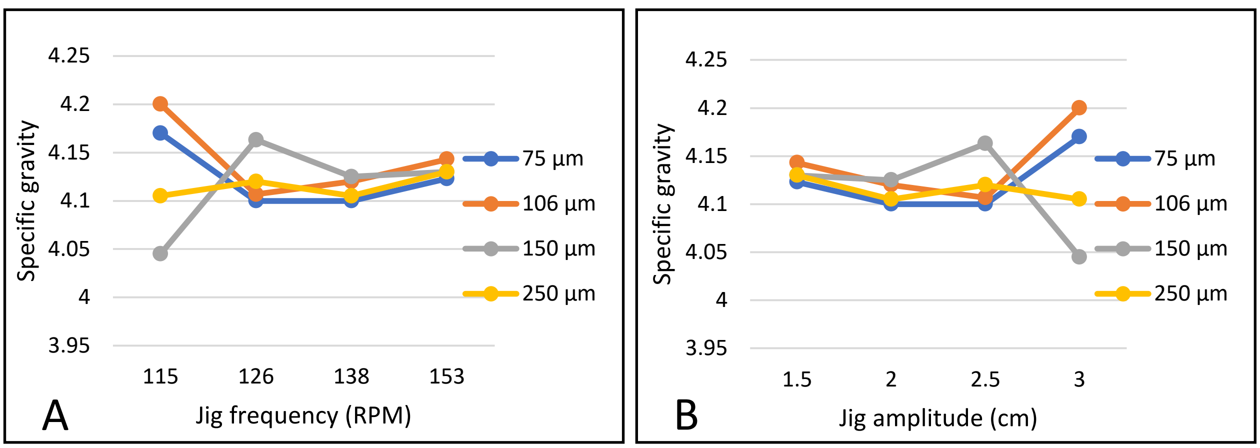


Figure 4.9: Specific gravities of jigging products as a function of (a): jig amplitude, and (b): jig frequency

4.4 Further Discussion

There are essential process parameters necessary for jigging to achieve jig concentrate of excellent quality. Before and during jigging, each mineral in the ore is liberated and free to ensure separation. Likewise, the individual mineral particle is fluidized when pulsed, becomes segregated, and separated. All these considerations affect the outcome of the current study and the entire jigging process. Thus, the overriding conditions examined within the study can be controlled efficiently to improve the quality of the jig tailings and concentrates.

In baryte ore deposits or ore (massive ore deposits), the value minerals are intimately locked and uniformly associated with gangue minerals (undesired minerals). The physical separation of each constituent within the ore depends on the liberation of valuable minerals (baryte and others) from the ore matrix. The baryte orebody's liberation is achieved by size reduction through crushing and grinding. In addition to the liberation of value minerals from undesired part of the ore deposits by size reduction, aggregates or lumps of sticky particles in a concentrated slurry is dispersed or broken using high-intensity and high-shear agitator. This is to ensure optimum separation of baryte and upgrading of its quality.

In the case of coarse jig feed, middlings, due to the association of value mineral with gangue minerals within the ore matrix, decreases the sharpness of minerals separation and lower separation efficiency. For fine or small-size particles, the formation of agglomeration of sticky particles or lumps or aggregates of solids in the slurry constitutes middling that has not been observed and discussed in previous research work (Nagaraj, 2000). Recent studies gave much attention to the engineering of jigging and the application of experimental results. However, there is a scanty discussion on the science of jigging that explains limitations to improving the separation efficiency of value minerals.

The solid-liquid mixture (slurry) of fine-fine and fine-coarse are usually influenced by higher cohesive interaction (Olhero & Ferreira, 2001). Similarly, the angle of repose changes, and the particle stability in the fluid is altered as the cohesive forces and capillarity bond increase due to increased fluid content. In the case of high solid loading, fluid viscosity increases, shear-thinning and thickening arise due to the rise in the volume of coarse and fine particles. A fluid-solid balance must be attained to achieve optimum viscosity that guarantees clogging of fine particles and better segregation. Moreover, better particle suspension/grain segregation of solids in fluids is experienced for a broader particle size distribution.

In the case of a complex mineral system (ternary where solids of different density and particle size exist), narrowing the particle size distribution provides better chances to segregate particles by reducing the contributing effects of interparticle forces, forces at the solid-fluid and fluid-fluid interfaces (Ferreira & Diz, 1992; Olhero & Ferreira, 2001). Given the above, the predominance of middling in slurry during jigging and its negative consequence on separation efficiency requires much attention.

4.5 Conclusion

In this study, jig separation of baryte ores of particle sizes less than 250 µm was carried out to examine the effect of mineral degree of liberation, jig frequency, and amplitude on separation efficiency using a laboratory-built mineral jig. It also evaluates the performance of locally-fabricated jig for processing baryte for artisanal and small-scale mineral processing. Results of the study show that a laboratory-built mineral jig is capable of small-scale processing of baryte ore for a weighting material in oil drilling mud. However, the sharpness of mineral separation was limited due to the occurrence of middling during jigging.

In line with the previous studies, the current work shows that coarse jig concentrate gave better mineral recovery and process yield. However, fine jig concentrates show better separation efficiency and retain less undesired minerals (impurities). Although some impurities have been removed, there is still a significant portion of quartz and hematite in the jig concentrate. Stage-wise or step-wise jigging of barite ore is recommended to ensure re-jigging of concentrate, recovery of value minerals in the tailings, and removal of gangue minerals from the concentrate.

The use of high-intensity and high-shear agitator within the jigging column to disperse or break aggregates of sticky particles in slurry during jigging will help reduce the influence of middling and improve the separation efficiency of value mineral during barite jigging. These devices can be incorporated in the laboratory-built design without depending on imported processing equipment for barite processing.

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5.0 CHAPTER FIVE: SAFE MINING ASSESSMENT OF ARTISANAL BARYTE MINING ACTIVITIES IN NIGERIA

5.1 Introduction

Mining is one of the world's most dangerous occupations (Amponsah-Tawiah et al., 2016). Over the years, many mining-associated accidents have occurred in various parts of the world, often with significant loss of life (Amponsah-Tawiah et al., 2016; Bringemeier, 2012; David Walters et al, 2014; De, 2021; Diwe et al., 2016; Donoghue, 2004; Duarte et al., 2019; Geng & Saleh, 2015; Le Berre & Bretesché, 2020; NIOSH, 2000). Such mining accidents remind us of how dangerous mining jobs can be and how explicitly hazardous underground mining continues to be (Hopkins & Maslen, 2015; Quinlan, 2014). Similarly, surface mining blasting-related risks (although not specific to underground mining operations) and their consequences could be worsened and may result in mass widespread accidents (Li et al., 2015; Mahdevari et al., 2014).

Mining accidents and fatalities among the Artisanal and Small-scale miners (ASMs) occur in the process of mining metals, minerals, and energy materials (i.e., not construction materials), as shown in Table 5.1. Thousands of miners die from these mining accidents each year, especially in coal and hard rock mining (Li et al., 2015). Although surface mining is usually less hazardous than underground mining (Bansah et al., 2016; Khanzode et al., 2011; NIOSH, 2000), the participation of artisanal and small-scale miners in barite mining fields has increased the number of mining fatalities across the upper and middle Benue Trough. Artisanal and small-scale mining (ASM) in Nigeria employed about 0.5 million as of 2015 (Oramah et al., 2015a), and in 2021 over 2 million. These miners' and mining communities' contribution to societal development is vital. Occupational and environmental health and safety issues must be objectively addressed at the mines and workplaces.

Table 5.1. Some cases of mining hazards in Nigeria.

Case Study	Damages/Sources/Causes	Remedy	References
Concentration of ^{226}Ra, ^{232}Th, and ^{40}K in mining dumps.	radiological hazards, high lifetime cancer risk index	No emerging medical health issues were observed. Regular medical Check-up of miners was recommended for early detection and treatment of potential health hazards	[20]
Concentration of Tl, K, Ca, Na and Mg in Au, Pb, and Zn mines' tailings.	High contamination index of Thallium, high ecological and health risks.	Remediation method was recommended, awareness creation	[21]
Concentration of 40K, 238U, and 232Th in tailings from granite mine.	Radiological hazard is within the permissible limit based on UNSCAR	Bioaccumulation/transfer factor level to be monitored	[22]
Concentration of air-borne lead and respirable silica from dry lead ore grinding and processing	high risk of lead poisoning, silicosis and tuberculosis	Wet spray misting used to reduce the mean airborne Pb and respirable silica	[23–25]
Concentration of Cu, Cr, Pb, Cd and Zn in iron ore tailings	serious non-carcinogenic health risk in children, high carcinogenic risk in adults.	research-industry- miners nexus was advocated	[26]
Concentration of As, Sn, Nb, Ta and Cd in surface water and mine tailings (alluvial) soil	moderate arsenic and cadmium Contamination and Geo- accumulation index (CI & GAI)	enforcement of environmental and mining laws to control pollution	

[20-26]=(Adeniyi JohnPaul Adewumi & Laniyan, 2021; Aluko et al., 2018; Anka et al., 2020; Daburum et al., 2019; Gottesfeld et al., 2019; Orosun, 2021; UNEP, 2011)

Heavy metal contamination due to mining and mineral processing (washing) has become one of the most silent but significant environmental side effects (Adamu et al., 2015b, 2015a). Studies in the literature have reported on acidification and acid mine drainage associated with the mining of coal, gold, and other minerals containing pyrite and galena (FeS_2 and PbS) (A. J. P. Adewumi & Laniyan, 2020; Laniyan & Adewumi, 2020). Baryte is one mineral or ore that has not been examined to pose such a threat (Adamu et al., 2015b). Baryte mineral, although non-carcinogenic, may be associated with lead sulphide (PbS) and encrusted with pyrite or iron pyrite microcrystal (Melekestseva et al., 2014; Szeleg et al., 2013). Sulphuric acid mine runoff is unavoidable when baryte tailings containing sulphide minerals are exposed to water and oxygen. The consequence is acidification of water and can increase the release of other heavy metals such as iron, zinc, copper, lead, cadmium, arsenic, and barium.

Previous reviews on safety and risk analysis have shown the relevance of workplace safety models in the safety-critical assessment of risks, either at mines or in any other activities where dangerous tools are used. Several safe assessment methods have been developed to address the quality and productivity of workers that sustain severe accidents at work and uncovered the adverse effect of heavy metal contaminants and other critical environmental threats to human health (Dunjó et al., 2010; G. Qin et al., 2021; Rezaie & Anderson, 2020; Bing Wang et al., 2018; Bo Wang et al., 2021). Researchers have examined ways to domesticate some of these advanced safe mining methods in Nigeria but with few positive results (G. Qin et al., 2021; Y. Qin et al., 2020; Rezaie A, Buresi M, Lembo A, Lin H, McCallum R, Rao S, Schmulson M, Valdovinos M, Zakko S, 2017; Rezaie & Anderson, 2020). This is because many local miners believe the “advanced” safe mining strategies have no direct correlation and cannot provide solutions to the type of mining hazard peculiar to them (Le Berre & Bretesché, 2020; Warra & Prasad, 2018).

Moreover, nothing much seems to have changed regarding miners’ and government attitudes to mineral exploration. Miners appear to have nothing to worry about despite the dozens of unreported cases of mining accidents. The significance of wearing safety kits such as mining boots, hand gloves, eye goggles, and clothes specifically designated for mining only at the site should be communicated again. There is also a claim that the institutional policy guilds' activities of artisanal and small-scale miners (ASM) caters to chemical contamination due to barite mining. However, the miners' and mining sites' managers are unaware of the safety data sheet, which is a minimum requirement for the operation of mines. Therefore, it is helpful to engage these local miners in discussing prevalent mining accidents and fatalities that have profound health implications and develop safe assessment methods, processes, and programs to prevent the reoccurrence of mining hazards.

This paper reviews mining activities by the artisanal and small-scale miners in Nigeria and presents safe mining strategies. It identifies mining accidents peculiar to artisanal and small-scale miners (ASMs), revises existing but weak and inadequate mining policy, and assesses potential mining risks to human health due to mining and social lifestyles of the miners. Questionnaires were administered to local miners (part-time and full-time) within the middle Benue Trough of Nigeria to identify hazards. Water from barite ponds and effluents was also analyzed to characterize associated risks and recommend safe mining protocols and controls, especially for the barite mining sector. Two research questions were investigated in the study. These are: (1) Certain mining accidents, and their adverse effect on miners are traceable to miners' refusal to use safe mining kits and (2) Artisanal barite mining contributes to severe heavy metal contamination. Field survey and heavy metal contamination assessment of water in baryte ponds and recycled wastewater at baryte mine sites validated the research questions.

5.2 A Review of Status of Artisanal and Small-Scale Mining (ASM) and Safe Mining Practices in Nigeria

5.2.1. Legal, Regulatory, and Institutional Frameworks of Artisanal and Small-Scale Mining

There are legal and regulatory documents and institutions that govern the activities of artisanal and small-scale miners in Nigeria. Figures 5.1 and 5.2 show the existing legal, regulatory, and institutional frameworks for Nigeria's mining sector. Aside from the frameworks, policy objectives guide the everyday activities within the mineral value-chain. These objectives include but are not limited to comprehensive actions on the acquisition of rights, mine ownership requirement and restrictions, minerals processing and export, transfer mineral rights, land use, environmental, mineral titles, health and safety, and constitutional law. Despite these frameworks, Nigeria's mining sector is yet to reach its full potential (Akper & Ani, 2020; Heffron, 2020; Macdonald et al., 2014).

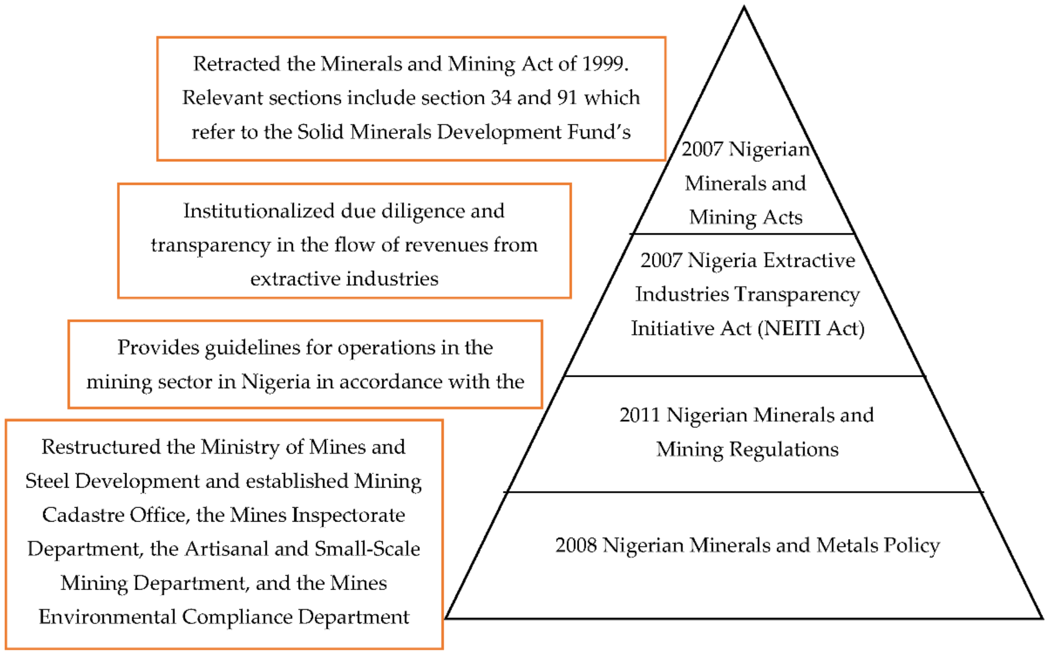

Figure 5.1: Legal framework for mining in Nigeria (adapted from (Ango et al., 2019)).

Figure 5.2: Institutional framework for mining in Nigeria (Modified from (Ango et al., 2019)).

Research has shown that enacting an Act and introducing laws or policies to drive Nigeria's mining sector can strengthen the regulatory frameworks (Akper & Ani, 2020; Ango et al., 2019; Heffron, 2020; Macdonald et al., 2014; Wireko-Gyebi et al., 2020). However, there were no prior works on health, mine safety, and mining hazard prevention procedures until March 2016, when the Nigerian government acknowledged mercury and lead (Pb) health risks. Mining accidents are not limited to chemical hazards. This set of rules is mandatory and must be enforced by every player within the mining and mineral business. It also includes every form of harm against the miners, mining communities, and resources located within the mining environment.

5.2.2. Mining Hazards in Nigeria

The sources of hazards associated with the sector include chemical, physical, and mechanical (Abdullahi et al., 2020; A. J. P. Adewumi & Laniyan, 2020; Atakpa et al., 2019; Järvholm & Silverman, 2003; JohnPaul et al., 2020; Kyari et al., 2000; Merem et al., 2017; Njinga & Tshivhase, 2019; Nwibo et al., 2012; Taiwo & Awomeso, 2017). Major mining accidents occur due to the use of crude and sharp tools by artisanal and small-scale miners to extract minerals. Some past and current mining hazards or accidents in different parts of Nigeria are shown in Table 5.2 and Figure 5.3. These hazards are traceable to the illegal mining and mineral extraction practices done by artisanal miners in Nigeria. Stone quarrying and solid minerals exploration dominate artisanal and small-scale mining (ASM) activities in Nigeria (Nwibo et al., 2012), as shown in Table 5.2 and Figure 5.3.

Table 5.2 Some mining activities and accidents in communities within the Nigerian States.

Mining Hazard/Accidents	Activities/Year	Locations	References
Air pollution (dusts, airborne Si, Ca), eyes damage asthma, damage to farm and cola-nut plantation	limestone quarry, cement production, lead mining (2013 till date)	Shagamu, Ewekoro (Ogun State), kalambana, Wumo, Kwakuti (Sokoto State), Ashaka (Gombe State), Jakura	[21]
Flooding, mysterious death, abandoned mines, contaminated lands, exposure to carcinogenic/radioactive substances.	Tin, columbite and clay mining (1960 till date)	Barkin-Ladi, Bukuru, Bossa, Riyom district (Plateau State).	[27]
Heavy metals water contamination, damaged ecosystem. airborne silica, land degradation	Coal, gold, and sand mining(2010–2013)	Enugu, Igun- Ijesha (Oguin State), Efikpo (Ebonyi State), Abeokuta, Owode, Ifo, Ado-Odo, Ofa, Ewekoro, Shagamu (Ogun State), Lagos State	[54]
Water and land degradation, pollutions	Marble mining (2010–2014)	Azara, Wuzue, Benu, Uywa, Lafia (Nassarawa) Luku, Minna (Niger State),	[54]

Death, mine collapse	Gold mining	Onyeama (Enugu State) Zawan (Plateau State)

[21, 27, 54]=(A. J. P. Adewumi & Laniyan, 2020; JohnPaul et al., 2020; UNEP, 2011)

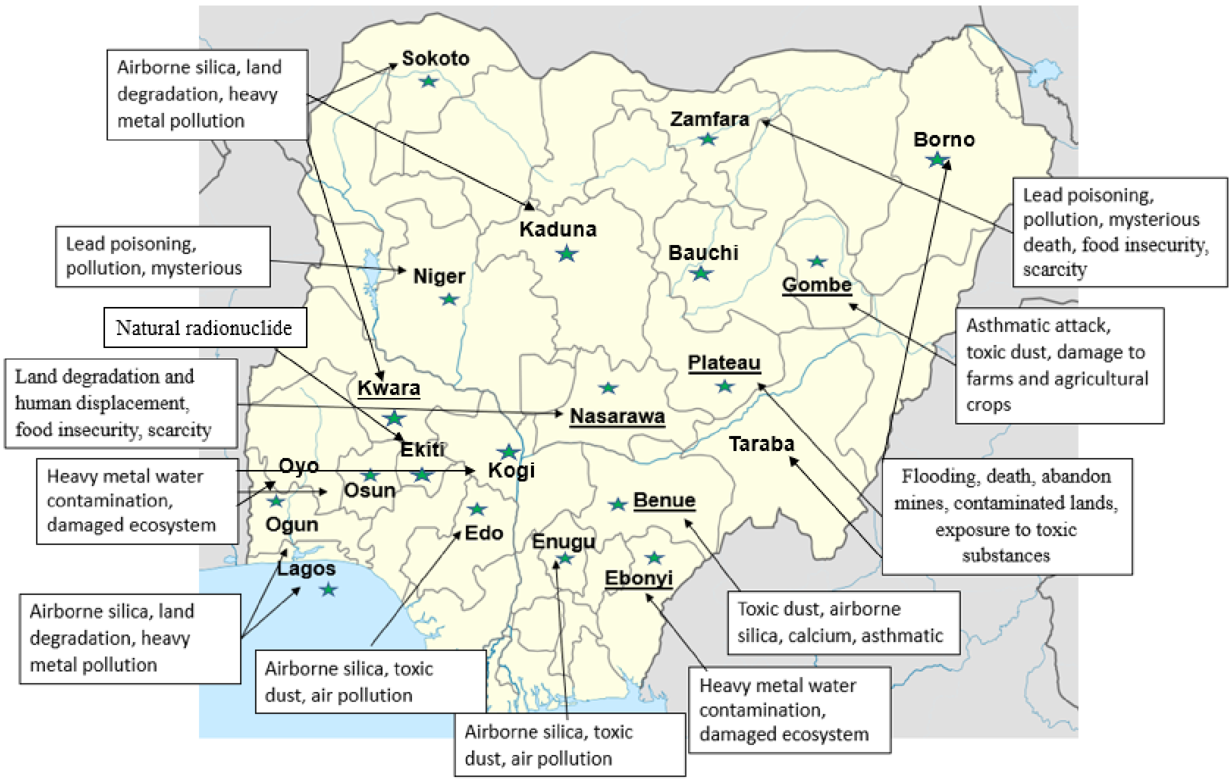

Figure 5.3: Mining Hazard Map of Nigeria (Anka et al., 2020; Dasgupta & Harrison, 1996; UNEP, 2011).

5.2.3. Safe Mining Methods for Local and Global Mining: Precautions and Control Measures

Within the last 25 years, there have been increased safety regulations, safer machinery development, training, and education initiatives for miners in Nigeria and Africa in general. However, this has not changed the fact that mining is still a dangerous profession (Amponsah-Tawiah et al., 2016). Before discussing potential accidents and risks in mining, it is vital to consider the average miner work shift based on human resource management. Typically, miners work in a 12 h shift at the underground mine while others work throughout the whole week or remain at a mining camp for months before returning home (Bansah et al., 2016). Miners are expected to be physically, mentally, and psychologically sound and healthy to achieve overall safety in mines. Strict adherence to safety procedures such as the use of respirators, ventilation systems, and ear protectors will go a long way to reduce cases of mining accidents, injuries, and fatalities (NIOSH, 2000). Some of the safety practices and challenges include those involving behavioural guidelines, communication, vehicle interactions, explosives, and the role of enforcement agencies (Akpan, 2005; Bansah et al., 2016; Denton et al., 2001; Frank et al., 2003; Manley, 2009; NIOSH, 2000; Orogbu et al., 2018; Zhong et al., 2020).

5.3 Materials and Methods

5.3.1 Survey of Miners

The state of hazards within the baryte mining industry was examined using surveying tools. Thirty-eight (38) unstructured questionnaires were distributed to miners who specialize in barite mining. Twenty-seven (27) out of thirty-five (~35) barite miners in the community completed and returned the questionnaires. The questionnaire was designed strictly as safety information-seeking procedures based on the primary objective of the safety training. The questionnaire also serves as a pre-training/pre-workshop tool or quiz used to identify and assess miners' health concerns and develop training manual(s)/choose efficient communication method(s) that address the peculiar needs of the miners under the study.

Approval for the research was obtained from relevant authorities. No medical procedures were observed, as no human body fluids or organs were used for any form of analysis or medical tests. The survey examines why miners refused to use mining boots, gloves, goggles, and clothes contained in the safety mining kits. The entire study attempts to assess and characterize potential health hazards caused by artisanal and small-scale mining (ASM) activities. Questions were read to miners who could not read.

5.3.2 Chemical Analysis and Risk Assessment

Quantitative risk assessment and health hazard analysis was done according to environmental standards and procedures. Water samples were collected from abandoned baryte ponds and wastewater from baryte washing and stored in polyethylene bottles (PET) at room temperature.

Two ml of the water samples were measured into the cuvette and filled to a mark. The dissolved elements in water samples such as Pb^{2+}, Ba^{2+}, Zn^{2+}, Fe^{2+}, and Cu^{2+} were analyzed colorimetrically using a Shimadzu UV-1900 UV-Vis Spectrophotometer. Tailings effluents was prepared in accordance with standards reported in (Ibe et al., 2016). The metallic content in the water samples was analyzed using atomic absorption spectrophotometer (AAS), Model: A-Analys 100. The liquid-liquid extraction method (LLEM) was employed in the absorption or digestion of the sample (Muller, 1969). The elemental composition of the samples was measured using PerkinElmer ICP mass spectrometer, NexION ™ 350X. The digestates of barite tailings or extracts were diluted to 1% (100 times).

The index of geoaccumulation (Igeo), contamination factor (CF), chronic daily intake (CDI), and health risk (HQ & HI) are computed for Pb^{2+}, Ba^{2+}, Zn^{2+}, Fe^{2+}, and Cu^{2+} using the data from the USEPA (United States Environmental Protection Agency) and DEA (South Africa Department of Environmental Affairs). Igeo, CDI, CF, and HQ were computed according to procedures reported in the literature. Each parameter was calculated using Equations (5.1)–(5.4) (A. J. Adewumi & Laniyan, 2020; A. J. P. Adewumi & Laniyan, 2020; Dasgupta & Harrison, 1996; A. B. D. EPA, 1989; U. S. EPA, 2004, 2016; Hakanson, 1980; Hessel GK, 1987; Shah et al., 2016).

$$Igeo = log_2 \frac{C_n}{1.5 \times B_n} \tag{5.1}$$

$$Contamination\ factor = \frac{Mean\ metal\ concentration}{Concentration\ of\ elements\ in\ background\ sample} \tag{5.2}$$

$$CDI\ \left(\frac{\mu g}{kg\ day}\right) = \frac{C_{MW} \times I_R}{B_W} \tag{5.3}$$

$$HQ = \frac{CDI_{non\ carcinogenic}}{RfD} \tag{5.4}$$

where C_n is the concentration of metal in water samples, B_n is the metal concentration in water before the introduction of metals due to mining activities, C_{MW} is the concentration of heavy metals in water, B_W, and I_R are the body weight and daily water ingestion rate, *HQ* is hazard quotient, *RfD*: reference dose factor, NOAEL: No-Observable Adverse effect level

5.4 Results

5.4.1. Characteristics of Survey Respondents

Figure 5.4 revealed the level of awareness of mineworkers about the minimum safety required during the mining operations. More than 92% of the miners surveyed were male, and ~64% of the miners who answered the survey were above 25 years old. It was clear that most miners are young adults, and over 50% of the barite artisanal miners in the study have only basic school education or had no formal education. The miners' biodata showed that many miners only understand local languages and may need to be trained on safe mining methods using local language to communicate essential details.

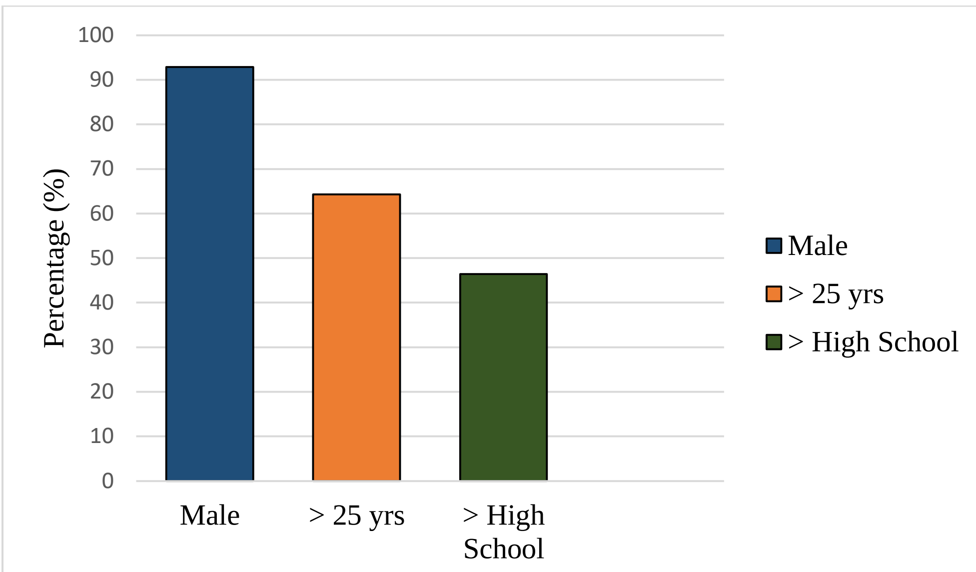

Figure 5.4: Characteristics of survey respondents (barite miners) showing human participation and performance at the barite mining site.

5.4.2 Health Hazards of Miners

Part of the survey sought to know the previous and present health challenges of miners within the barite field under the study. Figure 5.5 shows that ~54% of the miners that responded to the survey agreed they have health challenges traceable to illicit drug intake such as stimulants; 17.9% of the respondents had experienced specific symptoms such as headache, stomach-ache, body weakness, and difficulty breathing. Such health issues may be traceable to rigorous mining activities and exposure to poisonous substances (Babatunde et al., 2013; WHO, 2016). In comparison, 28.7% argued that they do not have any health issues. Also, 53.6% of the miners were ignorant of the benefits of using safety kits for mining, while 46.4% of the miners use safety kits but not at all times. Mine workers were exposed to certain risks, either knowingly or ignorantly, and become most vulnerable to sickness, air-borne diseases, and perhaps death because of insufficient knowledge about the risks associated with the mining profession.

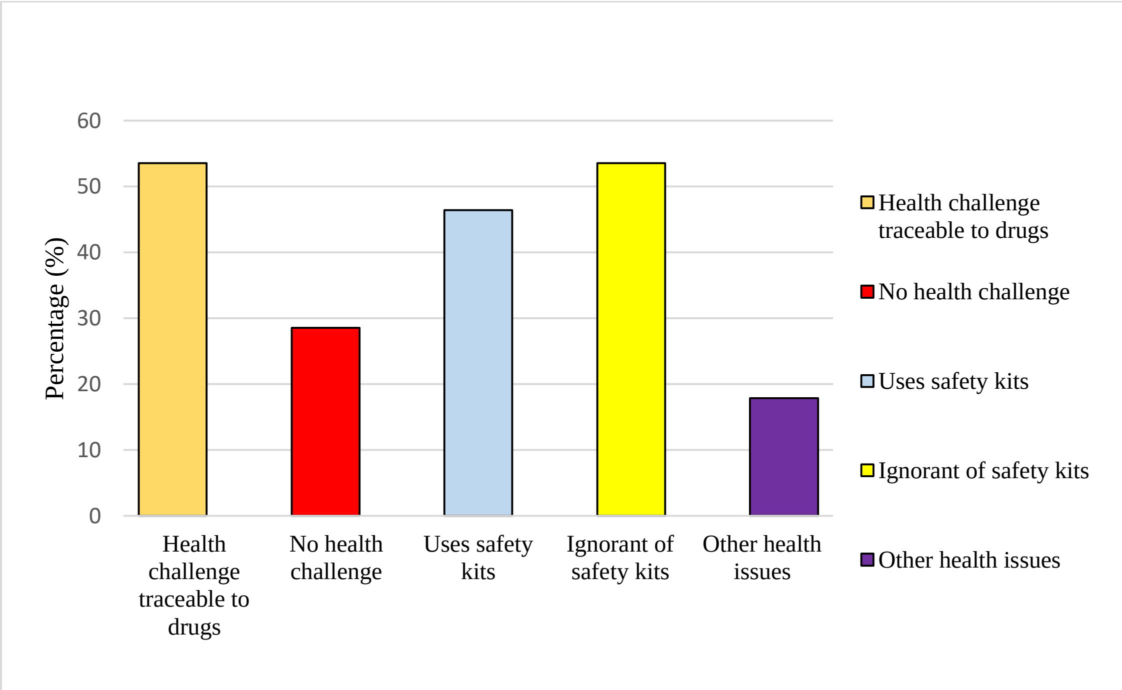

Figure 5.5: Health and safety issues in the mining sites under study.

Miners are subjected to long-time exposure to heavy metals contamination. Water used for washing minerals accumulates in ponds near the mining sites and are used for domestic purpose. Potential oral and dermal ingestion are assessed by analyzing water from baryte ponds and tailings.

The ultraviolent-visible (UV-Vis) spectra in Figure 5.6 identify absorbance bands showing the weak d-d transition of some identified transition metal complexes in the water samples. This indicates the formation of complexes of the transition metals in the octahedral fields as the d-orbital splits. The calibrated UV-visible spectrophotometer signifies and matches the transition metals in solution using the colour of the d-block compound. The peak absorbance wavelength of 675 nm is assigned to Cu^{2+}, and the visible absorbance band that stretches from 960–980 nm indicates electronic excitations for Fe^{2+}, V^{4+}, and Ni^{2+}. Similarly, the atomic absorption spectroscopy (AAS) identifies and measures the concentration of Zn^{2+}, Pb^{2+}, Cd^{2+}, Fe^{2+}, and Cu^{2+}, as shown in Table 5.3. The result indicates that Zn^{2+}, Pb^{2+}, Cd^{2+}, Fe^{2+}, and Cu^{2+} as transition metal ions may be present in the water samples associated with the mining site, as indicated by the baryte tailings. However, the concentration of copper and cadmium available in the site is less when compared with the World Health Organization (WHO) Standards or limits. The available concentration of lead and iron were 113.8 mg/kg and 15.6 mg/kg, respectively. In contrast, the WHO limits for these elements are pretty small, as shown in Table 5.3. Fe, Pb, and Cu exceed the WHO allowable limit and remain a potential threat to the mine workers and the host community.

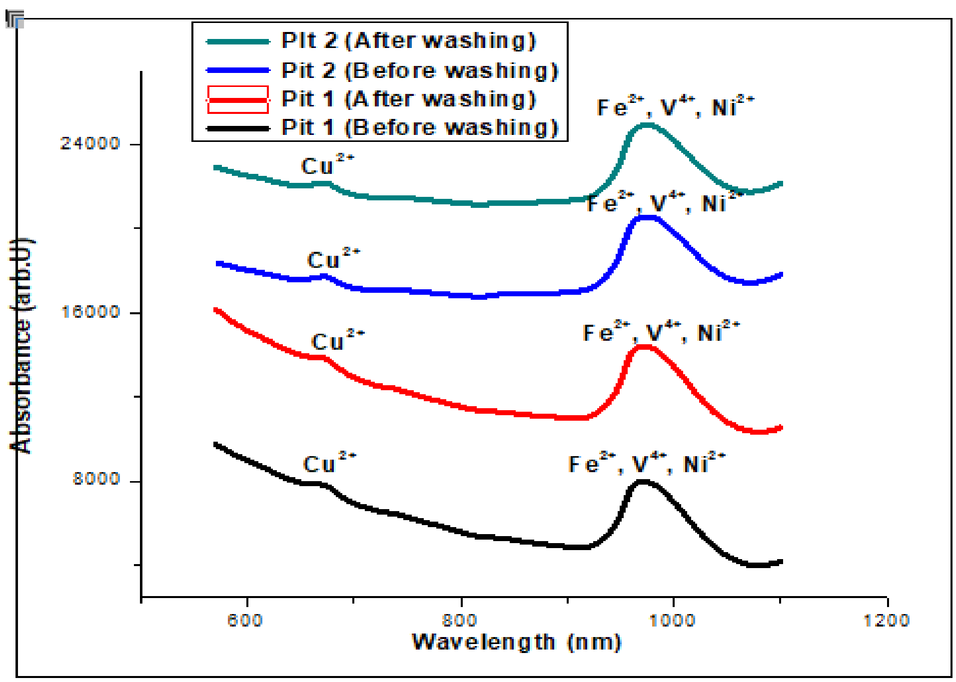

Figure 5.6: UV-Vis spectrograph for the elemental composition of water from the mined pits (UV-visible spectra of transition metals complexes identified in the water samples showing weak d-d absorbance bands at 675 nm and is assigned to Cu2+, and absorption bands that stretch from 960 to 980 nm posted to Fe^{2+}, V^{4+}, and Ni^{2+}, respectively).

Table 5.3 AAS analysis water sample TB (completely leached tailings) showing the concentration of heavy metals at barite mining sites in the Middle Benue Trough, Nigeria (Results were compared to WHO data in (Bansah et al., 2016; Donoghue, 2004)).

Heavy Metals	Proportion Baryte Mining Site (mg/L)	WHO Allowable Limit (mg/L)
Zinc	3.905	3.000
Iron	15.6094	0.300
Copper	0.3024	2.000
Lead	113.8127	0.010
Cadmium	0.0008	0.0030

The inductively coupled plasma mass spectroscopy (ICP-MS) results in Figure 5.7 shows that zinc, copper, and cadmium are below the maximum allowable limit set by World Health Organization (WHO), European Union (EU), Nigerian Industrial Standards (NIS), United States Environmental Protection Agency (USEPA), and China Ministry of Health National Standards (CMHNS) for ecological and health safety. However, the content of Fe in TB1 is relatively higher than the maximum allowable limits set by the governing standards. Similarly, Pb in TB1 is above the health and environmental risk levels recommended by the local and international agencies. This outcome indicates that the water used in the ore washing will result in water pollution and heavy metals' ingestion if returned to rivers and streams used by people. On the contrary, there was no evidence of cadmium contamination in the digestates of mine tailings or tailing effluents in the current study, as shown in Figure 5.7.

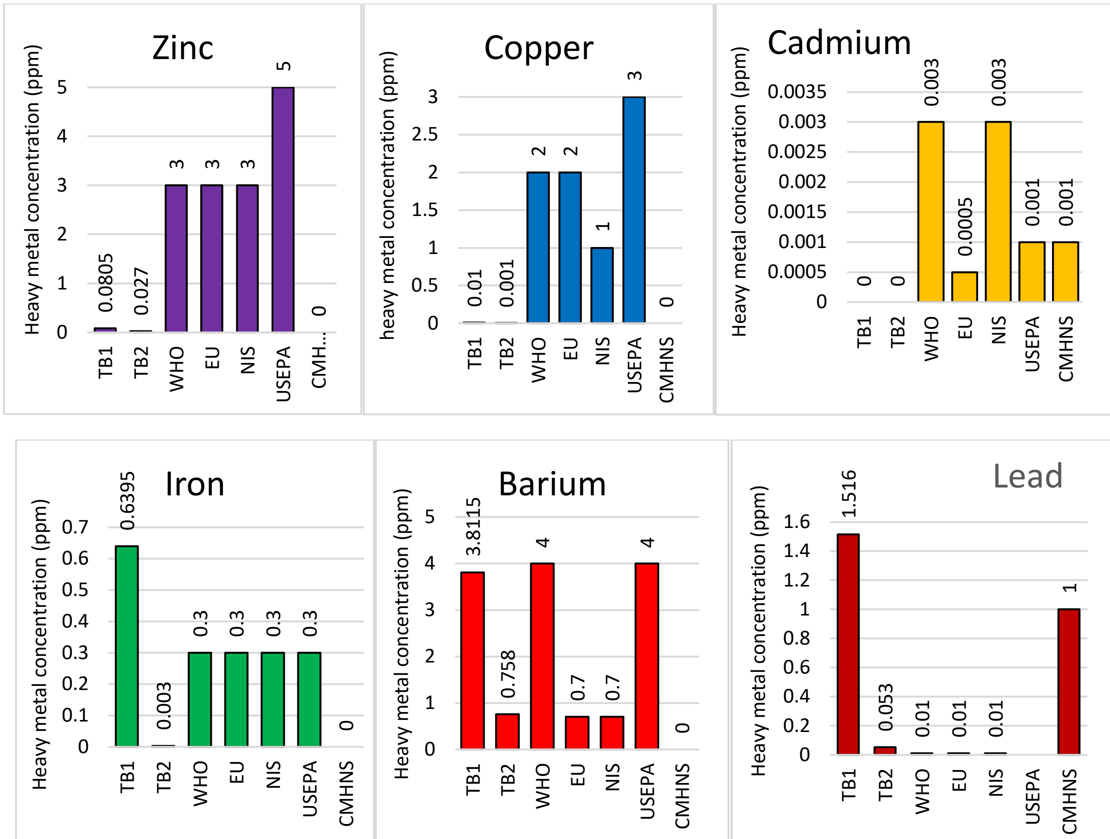

Figure 5.7: ICPMS Analysis. The concentration of heavy metals associated with artisanal barite mining (ABM) at some mining sites within the Middle Benue Trough, Nigeria.

WHO (World Health Organization); EU (European Union); NIS (Nigerian Industrial Standard); USEPA (United States Environmental Protection Agency); CMHNS (China Ministry of Health National Standards).

Contamination assessment of mine water samples in Table 5.4 shows that the index of geoaccumulation (Igeo) for Ba, Cu, and Fe in TB1 is between 0 and 1. Ba, Cu, and Fe moderately pollute barite ponds and rivers . Similarly, the Igeo of Pb in TB1 is above 6 (≥6). This indicates Pb extremely pollutes the ponds. The contamination factor (CF) of Ba in TB2 and Fe in TB2, Zn, and Cu in both samples are less than 1 (CF < 1). This implies that the water samples are lowly contaminated by Ba, Fe, Zn, and Cu and cannot pose any substantial risk to the health of miners and residents of the mining sites.

Table 5.4 Contamination Assessment of Heavy metals in mines water and tailing effluents.

Elements	Ba	Pb	Zn	Cu	Fe
(Igeo)					
TB1	0.344	7.659	–6.546	0	0.510
TB2	–1.985	2.821	–8.118	–10.966	–7.243
(CF)					
TB1	1.906	303.2	$\mathbf{1.61 \times 10^{-2}}$	$\mathbf{9.2 \times 10^{-3}}$	2.132
TB2	0.379	10.600	$\mathbf{5.4 \times 10^{-3}}$	$\mathbf{1.5 \times 10^{-4}}$	0.010
(CDI) Adult					
TB1	$\mathbf{4.47 \times 10^{-2}}$	$\mathbf{1.78 \times 10^{-2}}$	$\mathbf{9.45 \times 10^{-4}}$		$\mathbf{7.50 \times 10^{-3}}$
TB2	$\mathbf{8.90 \times 10^{-3}}$	$\mathbf{6.22 \times 10^{-4}}$	$\mathbf{3.17 \times 10^{-4}}$	$\mathbf{1.17 \times 10^{-5}}$	$\mathbf{3.52 \times 10^{-5}}$
(CDI) Child					
TB1	$\mathbf{4.17 \times 10^{-2}}$	$\mathbf{1.66 \times 10^{-2}}$	$\mathbf{8.82 \times 10^{-4}}$		$\mathbf{7.00 \times 10^{-3}}$
TB2	$\mathbf{8.30 \times 10^{-3}}$	$\mathbf{5.80 \times 10^{-4}}$	$\mathbf{2.95 \times 10^{-4}}$	$\mathbf{1.10 \times 10^{-5}}$	$\mathbf{3.29 \times 10^{-5}}$

On the other hand, the CF for Ba in TB1 and Fe in TB1 is between 1 and 2.999, and Pb in TB1 also exceeds 6 (>6). Pb moderately contaminates the barite ponds and other water resources. Also, the chronic daily intake (CDI) for Ba, Pb, Zn, Fe, and Cu in barite ponds or mine water and tailing effluents is between 1.17×10^{-5} mg/kg day and 4.47×10^{-2} mg/kg day for an adult, 1.10×10^{-5} mg/kg day, and 4.17×10^{-2} mg/kg day for children. The result presents the possible consequence of long-term exposure to heavy metals and classifies the toxicity level as acute or chronic.

Table 5.5 indicates that health quotients (HQs) of Zn, Cu, and Fe for the tailings (TB1 & TB2) are less than 0.1. Such HQ is classified as No risk (HQ < 0.1) and cannot lead to adverse health implications in a short time. The presence of Ba and Pb in TB2 poses a relatively low risk to health which shows that some precautionary measures should be taken to avert negative health consequences. However, Pb in TB1 contributes medium to high risk (for 1 < HQ < 4, and HQ > 4). Thus, an adverse effect non-carcinogenic risk is expected. Table 5.5 also shows that health indexes (HIs) of heavy metals in TB2 for adults and children are below 1. However, HIs for TB1 are greater than 1. For children and adults that drink up to 2 L of water from water sources contaminated by TB1, a cumulative HI of 5.81 indicates elevated non-carcinogenic risks (Table 5.5).

Table 5.5 Risk characteristics [Hazard Quotient (HQ) and health index (HI)] of Heavy metals in mines water and tailing effluents.

Elements	Health Quotient (HQ)					Health Index
	Ba	Pb	Zn	Cu	Fe	
(HQ) Adult						
TB1	6.39×10^{-1}	1.27×10^{1}	3.15×10^{-2}		1.07×10^{-2}	1.34×10^{1}
TB2	1.27×10^{-1}	4.45×10^{-1}	1.06×10^{-2}	2.94×10^{-4}	5.03×10^{-5}	5.83×10^{-1}
(HQ) Child						
TB1	5.97×10^{-1}	1.19×10^{1}	1.11×10^{-2}		4.91×10^{-3}	1.25×10^{1}
TB2	1.19×10^{-1}	4.15×10^{-1}	9.86×10^{-3}	2.74×10^{-4}	2.30×10^{-5}	5.44×10^{-1}

5.5 Discussion

The survey results shown in Figure 5.4 agree that artisanal baryte mining is dominated by men (mostly young adults) and has a lower literacy level as reported on the general status of artisanal and small-scale mining (ASM) in Nigeria. Previous research has shown that artisanal miners of gold, gemstones, diamond, galena, limestone, zinc have similar gender distribution and are exposed to peculiar risks and difficult tasks associated with their profession. Miners are predominantly unskilled and semi-skilled, as observed with artisanal miners specialising in gold, gemstone, granite, and sand mining. This agrees with the general state of several mining sites managed by artisanal and small-scale miners in Nigeria (Ahmed & Oruonye, 2016; Melodi & Opafunso, 2014; Nwagwu et al., 2015; Olley, B.O; Abikoye, 2016; Oramah et al., 2015b; Tirima et al., 2016).

In the current survey, it was quite true that some of the miners felt their present medical conditions are due to factors other than mining, as shown in Figure 5.5. Several works reported in the literature have shown that all miners are vulnerable to mining hazards aside from previous medical conditions, except those using complete protective kits during mining (Nwibo et al., 2012; WHO, 2016). Artisanal miners are exposed to dust risk, which lowers the Forced Expiratory Volume (FEV) and Forced Vital Capacity (FVC). Such results have shown that miners that abuse drugs as stimulants may not experience reduced lung function (fibrosis), defective oxygen diffusion, and impaired pulmonary function in the short term. However, exposure to heavy metal contamination would further worsen the present medical conditions

(Azodo & Omuemu, 2017; Esheya et al., 2017; Nwibo et al., 2012; Oramah et al., 2015a; Ralph et al., 2018; WHO, 2016).

Post-survey discussion with miners reveals that artisanal barite miners do not have the financial capacity to fund bills of medical examinations. Most artisanal miners earn lower than the cost of medical treatment. They would prefer self-medication or a traditional medical practitioner for medical consultation and treatment as no medical facilities and personnel available. Miners illicitly use nicotine to fight body weakness and other symptoms that require an adequate medical examination. Also, it is uncertain whether owners of mining sites offer medical care to miners as there is no part of the mining policy or institutional frameworks that compelled or enforced employers to provide for the medical care of miners. Miners are encouraged to use safety kits during mining and seek medical attention when necessary. The need for annual medical outreach to mining sites is recommended for medical counselling, diagnosis, treatments, and referral of miners with severe medical conditions to access medical facilities.

High values of HQs for Ba and Pb increase HI's value for water sample TB1. However, the case is different for sample TB2, posing no observable hazard to human health. The use of such water for various applications and eating aquatic lives such as fishes loaded with heavy metals is unsafe. Also, the heavy metal contamination risk assessment revealed that water from barite ponds and wastewater returned into the river are contaminated by lead and barium. The chronic daily intake (CDI), health quotient (HQ), and health index (HI) for these heavy metals in the water samples suggest that an adverse effect due to non-carcinogenic risk is expected. The use of affordable water filters such as carbon filters specifically designed to remove lead and Ba will help to reduce the quantity of heavy metals consumed in drinking water.

5.5.1 Major Inhibitors to Safe Mining Methods in Nigeria

The foremen, managers, and owners of mining sites, mineral processors within the mining industries, and academia, as stakeholders, were interviewed verbally to identify major inhibitors to safe mining in Nigeria. The inhibitors identified include funding, lack of enforcement, infrastructural needs, and insecurity.

Project Funding: The Nigerian government has done a lot through the Federal Ministry of Mines and Steel Development (MMSD) to reform of institutional framework, establishment of ASM

Directorate, Solid Minerals Development Fund (SMDF), Mineral Sector Support for Economic Diversification Project. However, some of the stakeholders in the industry and research institutions complained that funds for the projects hardly get to the mine inspectors to develop safety procedures and protocols.

Regulations and Sanctions: Although many regulations and sanctions have been established, implementation has been lacking. Mine inspectors hardly visit mine sites, and minimal awareness is created among the miners on safety and health hazards.

Infrastructural Collapse and Decay: The infrastructural imbalance within the country has completely paralyzed the power, transportation, mines, and minerals sector of the economy. However, the outright privatization of electricity generation and distribution and rail transportation should encourage investments in mining equipment importation for local mineral beneficiation and development of mines.

Security and illegal mining: Most recent and ongoing security challenges within the middle belt, Northeastern and Niger-delta regions of Nigeria can be addressed by developing a robust corporate social responsibility program to alleviate the suffering of the people living within the mineral mining and processing communities. The enactment of the mining act and collaborations among the foreign investors and experts will assist the Nigerian government in the development of a workable mining framework and a road map significantly required for relevance within an acceptable safe mining operation (Bansah et al., 2016; Kalu, 2020).

5.5.2. Impact of COVID 19 on Health of Miners

The first official case of the coronavirus disease 2019 (COVID 19) pandemic was announced in Nigeria on February 27, 2020 (Adebowale et al., 2021; Kalu, 2020). In the advent of the COVID-19 pandemic, Nigeria’s mining industry experienced sudden downtime, reducing its contribution to the national gross domestic product (GDP). The recent drop-in commercial activities and demand for minerals has also worsened the situation. Also, cohorts of individuals face health and financial challenges during the pandemic. Aside from the older people, miners and mining community’ respiratory health is at stake because some miners have pre-existing medical complications (Amzat et al., 2020; Ralph et al., 2018; WHO, 2016). There is, however, no specific data or literature on incidents of COVID 19 related cases or the death of miners. Other subsidiary concerns among the artisanal and small-scale miners, who do not have a stable income for feeding and medical tests, surround the ability to continue routine medical examination and treatment during the pandemic. Therefore, the participation of private health providers and global aid agencies is critical at this point.

In the real sense, the right time to implement innovative and strategic plans, cultivate safety information-seeking behaviour in artisanal and small-scale miners (ASMs), and enforce safe mining practices to ensure that miners and the mining activities are safe, is now. Such plans are not limited to remote collaboration, adoption of digital capabilities, safety training on the use of safe mining kits, strict observance of work ethics, occupational and environmental health safety protocols, and personal hygiene in addition to local CDC protocols on COVID-19 prevention, and vaccination of miners. Also, in collaboration with the Capstone team in the United Kingdom, the Nigerian government is reassessing the existing roadmap for mineral exploration amidst new challenges and opportunities due to the pandemic (Afolayan et al., 2021; Ango et al., 2019; Nwagwu et al., 2015).

5.5.3 Policy Imperatives and Strategies for Fostering Safe Mining

Mining in Nigeria is regulated by the Constitution of the Federal Republic of Nigeria, 1999, and the Nigerian Minerals and Mining Acts, 2007. The Nigerian Minerals and Mining Regulations, 2011 are the applicable regulations and policies that control the artisanal and small-scale mining (ASM) activities in Nigeria. These policies directly address mineral exploration, environmental protection, and safety (Mallo, 2012; Mensah et al., 2015; Oramah et al., 2015a; Saleh & Cummings, 2011). Policies on the environment, health, and safety have been the focus of this study. Although laws should enforce strict observance of these policies for all miners, only legal holders of mineral titles can be tracked. There are reports on Nigeria's government effort to formalize over 1.5 million artisanal and small-scale miners (ASMs) into cooperative groups (Ango et al., 2019; Mensah et al., 2015). However, information available to miners is limited.

Mine Inspectors and Mine Cadastral Officer are responsible for information dissimilation, but their ratio to ASMs is about 1:200 to 1:10,000. There is an urgent need to strengthen information aids and sources to formalize artisanal and small-scale miners in Nigeria. An information-sharing framework can be supported by government declaration for a Miners' Day, a public holiday entirely given to massive sensitization on safe mining issues, safety education and awareness, medical outreaches, and miners networking. Considering mining as a hazardous endeavour, formalizing ASMs into groups will ensure adequate operations management and encourage the participation of relevant stakeholders such as Medical Doctors and Paramedics, rock mechanics, and mining engineering experts. Given the above, existing policies should guarantee safe mining at all mining sites in Nigeria.

A generalized future mining plan in Nigeria called Nigerian Mining Road Map exists, but the content only speaks to the public without any commitment to ensure its compliance. As earlier mentioned, owners of mining sites and the government are more concerned with the business of mining and not the quality of mineral extraction, safety of life, and the mining environment. The road map proposes the path to mining prosperity and not to ensuring a responsible and sustainable mineral extraction. However, as part of the plan to diversify the economy due to the pandemic, the Ministry of Mines and Solid Minerals Development (MMSD) considers using Science and Technology in solid mineral exploitation. This includes the use of satellites for mining data acquisition for solid mineral exploration and Artificial Intelligence (Al) to ensure mining safety and efficiency of mineral processing methods. There is a need to adopt an automated safe mining strategy or incorporate mine-based technology such as mine remoting and an automated mining system. This is key to envisioning sustainable barite mining; however, a stable power supply (electricity) is needed to drive this technology contained in the mining road map.

5.6 Conclusions

This study identifies and reviews mining accidents peculiar to artisanal and small-scale mining (ASM) to re-iterate that mining accidents have severe consequences on miners and their environment. It revises existing but weak and inadequate mining policy, assessing potential mining risks to human health due to the mining and social lifestyles of the miners. Results show that artisanal miners are exposed to polluted water, air, and farmland. The consumption of water from barite ponds poses a relatively high risk to human health over a long period. Therefore, it can be concluded that mineworkers are exposed to a certain level of risks either knowingly or ignorantly due to artisanal barite mining. Adverse non-carcinogenic risks due to Pb and Ba in water and a worsening of health via illicit drug intake are expected. Operational therapy and practices such as sensitization on the danger of drugs to health, the importance of sufficient rest, and the use of safety tools and affordable water filters have been recommended to ensure safer artisanal mining activities. To envision the future of barite mining, detailed recommendations on the need for annual medical outreach to mining sites and the use of technology (Al) for future mining were presented. Some peculiar safe mining protocols and controls to reduce the daily chronic intake (CDI) of heavy metals in water (barite pond and tailings) are also mentioned.

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6.0 CHAPTER SIX: PHYSICOCHEMICAL STUDIES FOR RISK IDENTIFICATION, ASSESSMENT, AND CHARACTERISATION OF ARTISANAL BARITE MINING IN NIGERIA

6.1 Introduction

Mining and processing of minerals have a significant impact on economic well-being in several ways (Amponsah-Tawiah et al., 2016; Bansah et al., 2016; Khanzode et al., 2011). The abundant supply of cheap labour, limited availability of capital, lack of advanced methods and technologies for mineral exploitation, and poor existing transportation networks, together with an urgent demand for minerals both within the continent and abroad, have led to the rapid establishment of mining activities, without due consideration of many types of consequences (Afolayan, Adetunji, et al., 2021; Afolayan, Onwualu, et al., 2021). Nigeria and most countries in Africa have not attained their full potential in mining hazard and fatality response management. This is due to the lack of capital and technological means to identify mining hazards and to assess and characterize potential risks to human health as is necessary to improve the safety of the miners (Afolayan, Adetunji, et al., 2021; Agwu & Olele, 2014; Stemn, 2019).

Recently, the Nigerian government has identified seven strategic minerals for attention and has proposed a ban on their importation to help stimulate the local mining industry and improve the nation's economic prosperity (Fayemi, 2016). These include coal, Fe ore, bitumen, gold (Au), limestones, lead-zinc (Pb-Zn), and baryte (Fayemi, 2016). However, an enabling environment for mining these strategic minerals remains a major concern. Baryte ore, among others, contains non-barite minerals with associated metals such as Pb, Zn, Sn, Cu, Cd, Fe, and others (Gottesfeld et al., 2015, 2019). These elements and compounds constitute a threat to mining communities' health and well-being during mining and mineral processing (Adeniyi JohnPaul Adewumi & Laniyan, 2021; Afolayan, Onwualu, et al., 2021). Massive barite deposits are formed along river beds, and the mined pits are usually submerged with water. Overflow from these pits finds its way into major streams within the mining communities, flooded to cover a wider area around the river bank during the wet season, as shown in Figure 6.1 (Afolayan, Adetunji, et al., 2021; Oden, 2012). The barite pits serve as ponds for fishing, and their water is used for bathing, drinking, washing clothes, and harvesting crops during the dry season.

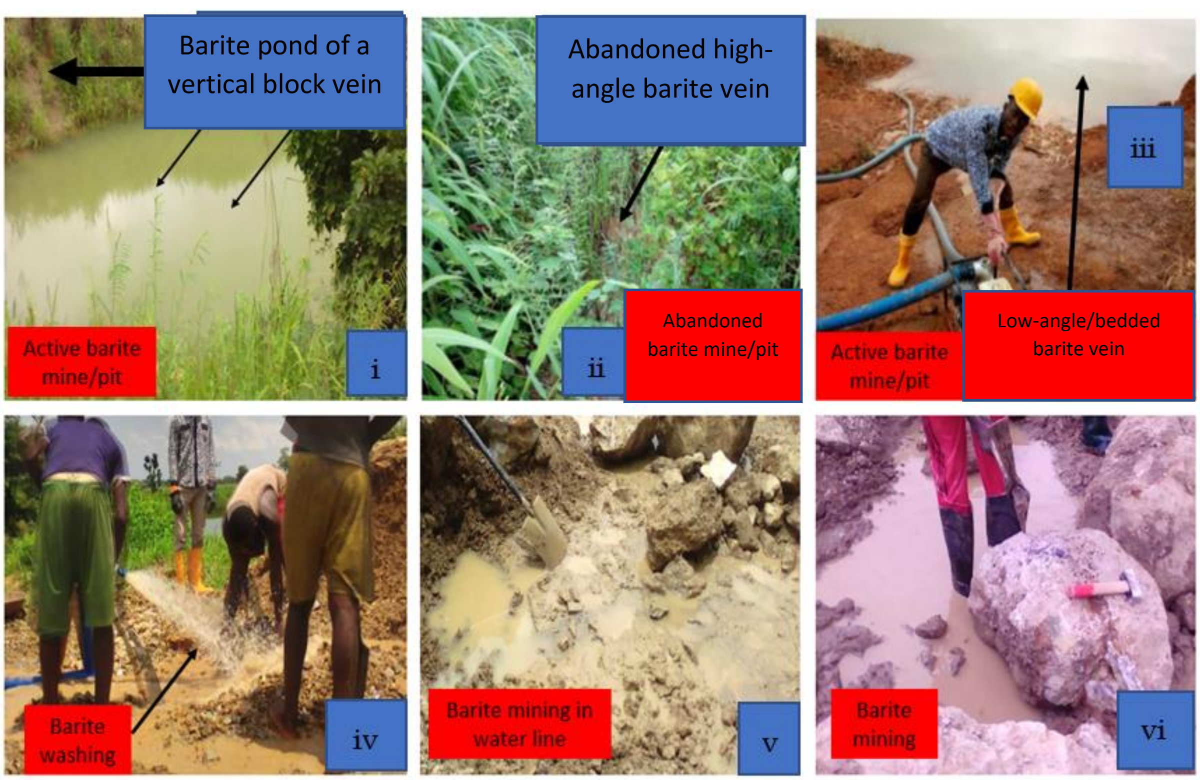


Figure 6.1: Baryte mines and mining activities at baryte fields under study ((i–iii): active and abandoned barite pits in Nigerian baryte fields, (iv-vi: washing and pre-processing of baryte ores).

Several works have examined and analyzed heavy metal contamination of water and the environment due to geologic and anthropogenic activities such as artisanal mining and mineral extraction activities (A. J. Adewumi & Laniyan, 2020; Alam et al., 2019; Gottesfeld et al., 2015, 2019; Hadzi et al., 2019a; L K. Boamponsem et al., 2010; Oden, 2012; Wang et al., 2012) and other sources (Olaifa, F.E., Olaifa, A.K., Adelaja, A.A. and Owolabi, 2004; Oluwatuyi et al., 2020a). Such research focused on the determination of ecotoxicity levels in soils, arable crops, vegetables, aquatic lives, and the environment and assessed health hazards due to mining at gold, Pb-Zn-F, coal, granite, silica/sand, Pb, Fe ore, and barite mines (A. J. Adewumi & Laniyan, 2020; Ajiboye et al., 2016, 2018; Aluko et al., 2018; Anka et al., 2020; Dike et al., 2019; Donoghue, 2004; Dudek et al., 2020; Gholami et al., 2020; Guo et al., 2021; Hadzi et al., 2019a; Laniyan & Adewumi, 2020b; Macdonald et al., 2014; Njinga & Tshivhase, 2019; I Ochelebe et al., 2020; Ibu Ochelebe et al., 2020; Wang et al., 2012). However, scientific information about heavy metal contamination and the danger imposed on human lives and the environment due to baryte mining is still often unknown and reliable data relatively scarce (Afolayan, Onwualu, et al., 2021).

Research articles in the literature on heavy metal contamination due to baryte mining primarily have emphasized the toxicity of heavy metals other than barium (A. J. Adewumi & Laniyan, 2020; A. J. P. Adewumi et al., 2020; Adeniyi JohnPaul Adewumi & Laniyan, 2021; Alam et al., 2019; Daburum et al., 2019). Studies on the heavy metal contamination due to baryte mining focused on commonly known heavy metals such as Pb, As, Mn, Cr, and Cd. Research works similar to the present study focused on the hydrochemical analysis of water samples from ponds and rivers close to baryte mines and human health risk assessment (Christopher Iorfa Adamu et al., 2014; Laniyan & Adewumi, 2020a). These few pieces of work also presented valid safety assessments of baryte mining based on local and national health and environmental standards (Drochioiu et al., 2016; Ebunu et al., 2021; Ibu Ochelebe et al., 2020). This work may be sufficient if baryte mining in Nigeria and Africa is carried out by local investor-backed companies following environmental best practices. However, baryte, like any other minerals of interest, is mined by artisans and operated informally (C I Adamu et al., 2015; Afolayan, Adetunji, et al., 2021; Brenniman et al., 1979; Ebunu et al., 2021; Otoijamun et al., 2021). Barium dosage above 4 g/day can cause acute diseases and is dangerous to the entire ecosystem's well-being over a long time (Christopher Iorfa Adamu et al., 2014; Brenniman et al., 1979; Brenniman & Levy, 1984; WHO, 2001, 2004). Baryte mineral, although non-carcinogenic, may be associated with lead sulfide (PbS) and encrusted with FeS_2 or Fe-FeS_2 microcrystals. Sulfuric acid mine runoff is unavoidable when baryte tailings containing sulfide minerals are exposed to water and oxygen (Christopher Iorfa Adamu et al., 2014; Drochioiu et al., 2016; Melekestseva et al., 2014; Szeleg et al., 2013). Thus, it is necessary to assess the poisonous level of barium as a heavy metal that forms part of the total toxic index to ensure the safety of miners, mining communities, mammals, and the entire ecosystem. The knowledge generated will be useful for modifying ASMs in Nigeria.

This work identified heavy metal contaminants in mine water samples and effluents of baryte tailings randomly selected from three baryte mining sites in Northeastern and Northcentral Nigeria. It examined the contribution of ASMs in baryte mining and extraction to water contamination/pollution with and without the interference of any geologic processes (erosion, landforms, depositions, and weathering processes). The extent of pollution caused by artisanal mining activities and its consequences for the ecosystem and human health were assessed.

6.2 Materials and Methods

6.2.1 Sample Collection, Chemical Digestion, and Analytical Methods

Baryte rocks were randomly sampled from Ibi, Wase, and Kumar barite sites (not less than 15 baryte rock samples were taken from each site between July and September 2019). These were pulverized and digested using 2 mL of hydrochloric acid (98%), 10 mL of sulfuric acid (97%), and 5 mL of nitric acid (68%) (Lab Alley, Spicewood, TX, USA; Palmer Eldritch, USA; Alliance Chemicals, Taylor, TX, USA). These samples were filtered to remove non-soluble particles and labelled as KB1, IB1, WB1, KB2, IB2, and WB2. Digestates (filtrates of the digested samples) of baryte tailings (tailing effluents) and powder samples were analyzed using ICP-MS. Chemical absorption and digestion of samples were performed at the Environmental and Water Research Laboratories, Civil and Environmental Engineering Department, Worcester

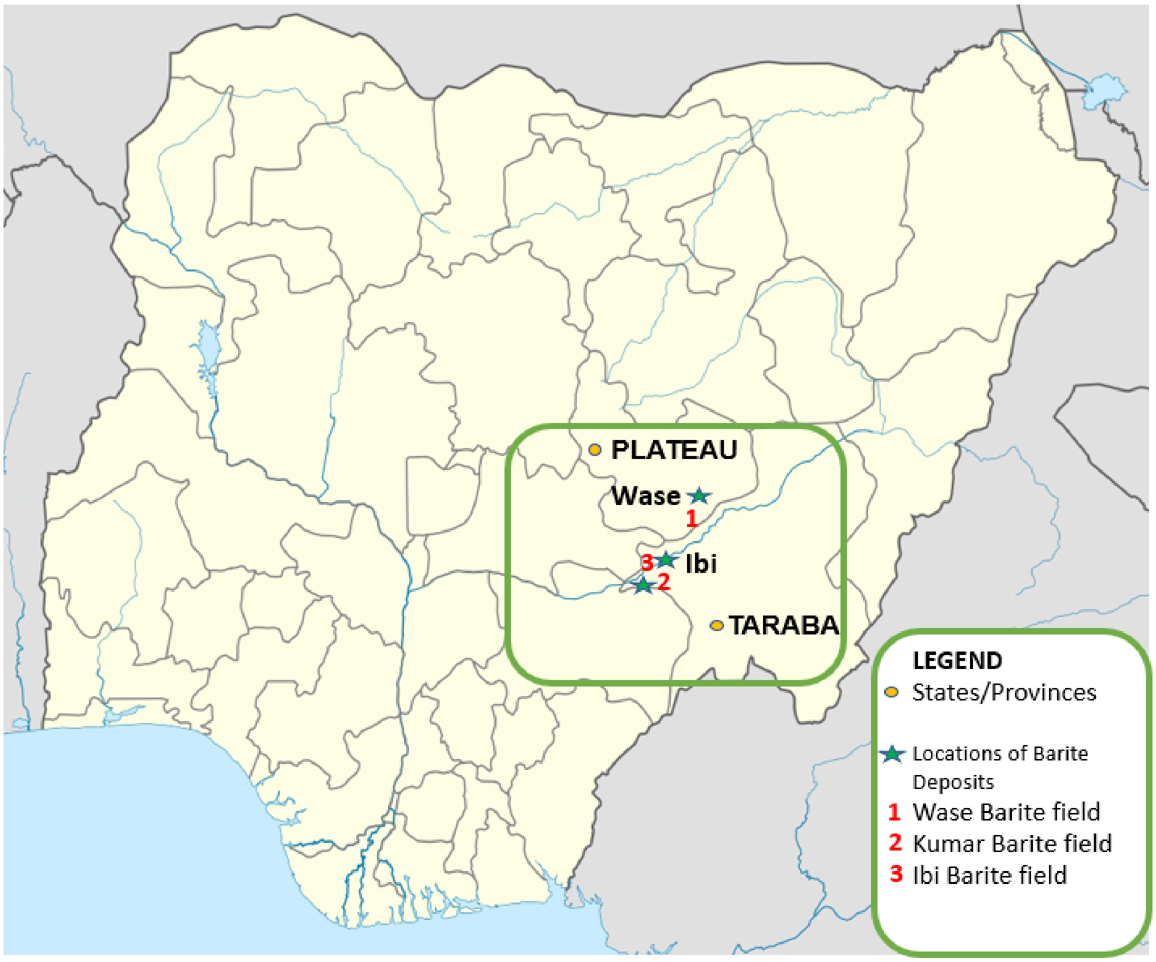
Polytechnic Institute, USA. Similarly, tailing effluents and water samples were analyzed at the Wole Soboyejo Biomaterial Laboratories, Worcester Polytechnic Institute, USA.

The safety of baryte mining was assessed by comparing the heavy metal concentration in mine water and tailing effluents with environmental and health standards (World Health Organization (WHO), European Union (EU), Nigerian Standard for Drinking Water Quality (NSDWQ), Nigerian Industrial Standard (NIS), United States Environmental Protection Agency (US EPA), and China Ministry of Health National Standards (CMHNS)) (Agency, 2006; Brenniman et al., 1979; U. S. EPA, 2004, 2016; Melekestseva et al., 2014; NIS-554-2015, 2015; WHO, 2004). This study was limited to analyzing mine water samples and digestates of mine tailings from the abandoned and active mining sites. Thus, no medical examination was performed as part of this study.

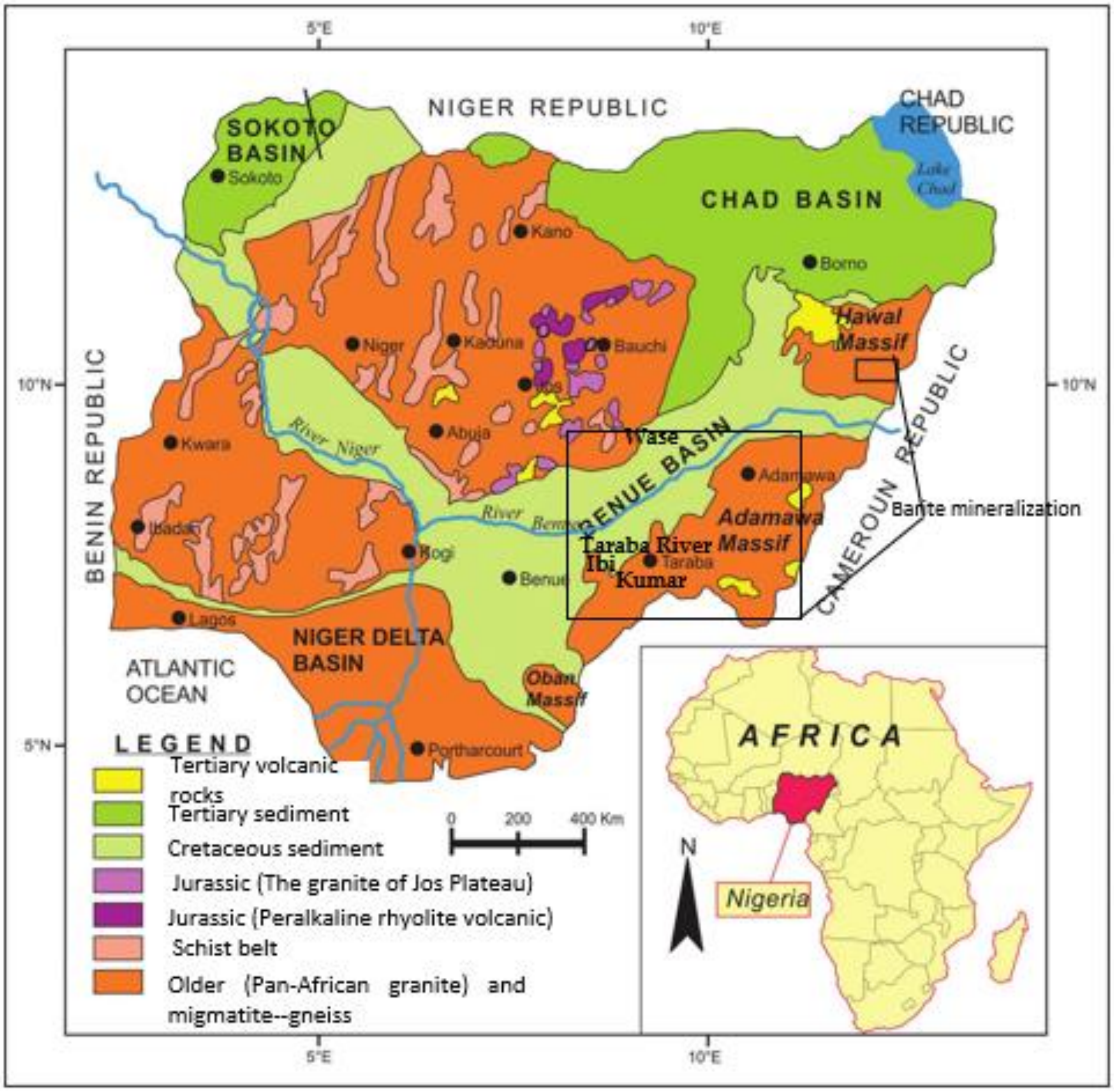
6.2.2 Site Description

The mineralized zone of the Nigerian Benue Trough consists of the upper, middle, and lower divisions. The central geological structure forms part of the broader West and Central African Rift System within the Trough. During a series of Cretaceous stages, these activities led to the formation of mineral deposits overlaid with Tertiary and more recent sediments. The Trough was formed by rifting the central West African basement, beginning in the Cretaceous period, and accumulated sediments deposited by rivers and lakes as shown in Figures 6.1 and 6.2 (Aladesanmi, 2018; Aliyu et al., 2015; Ekwueme et al., 2015; Ekwueme & Akpeke, 2012; EL-Nafaty et al., 2015; N A Labe et al., 2018; Ngukposu A Labe et al., 2018; Oden, 2012; Offodile, 1976; Ogundipe, 2017). The basin subsided and was covered by seafloor sediments accumulated under oxygen-deficient bottom conditions during the late early to middle Cretaceous. As the southern Atlantic Ocean started to open up in the Cretaceous, sedimentary rocks formed in the rift valleys, and volcanic rocks such as basalt occurred along the edges of the rift. These igneous–metamorphic rock mixes are hosts to minerals such as baryte, calcite, galena, hematite, magnetite, and a host of others (Ngukposu A Labe et al., 2018; Oden, 2012; Offodile, 1976).

The middle section of the Trough contains several baryte veins formed at the late early to middle Cretaceous and toward the end of the Cretaceous. The veins formed in the first phase of deformation vary in quality due to the presence of non-baryte minerals (Oden, 2012; Offodile, 1976). The current study characterized sources of health hazards traceable to heavy metal contamination caused by barium and other non-barium metals in barite tailings and ponds at Ibi, Wase, Kumar, and other selected barite fields, as shown in Figure 6.2a & 6.2b.



(a)



(**b**)

Figure 6.2: (a) Map of Nigeria showing the study areas. (b) Simplified geological map of Nigeria showing the igneous and metamorphic outcrops of the Precambrian Basement Complex, other rocks as major aquifers, water reserves, and some spotlights of barite mineralization within the study areas and other extended mineral ore concentrations (modified/adapted from (Salawu et al., 2020)).

An equatorial climate characterizes the baryte mining sites with dry and wet seasons and an average daily temperature between 25°C and 35°C across the year (Ankidawa et al., 2020;

Gabriel et al., 2020). The wet season usually covers April to October, with the mean annual rainfall between 1000 mm and 1350 mm. There are ferruginous tropical and alluvial soils (classified as Ferric Luvisol and Fluvisols), derived from the crystalline acid rocks of the basement complex (Gabriel et al., 2020). Moreover, with the the Benue and Taraba Rivers as the major basin, the area is heavily subjected to gullies and massive flooding due to natural events (hazards) and anthropogenic activities (barite mining).

Wase site is characterized by quaternary sedimentary deposits and weathered and tectonically fractured zones of crystalline rocks. Groundwater circulation occurs partly through fractured crystalline and volcanic rocks and partly within alluvial, eluvial, colluvial, and chemically degraded deposits. These aquifers host and distribute soil water and are disturbed by mining activities. Mining excavations, drilling, and open and blasted wells create direct access to groundwater. They are contaminated by the oxidation of abandoned mine tailings, leaching of heavy metals, and drainage of materials from active and abandoned mines (Akujieze et al., 2003; Diloha et al., 2018; Gyang & Ashano, 2010; Laniyan & Adewumi, 2020a). Thus, the groundwater, which is a major source of freshwater within the mining areas, is distributed based on the volume of rainfall, streamflow, weathering and mining activities, and the texture and structure of the rocks.

6.2.3 Characterization of Mine Water Sample

6.2.3.1 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) Analysis of Water Samples

The elemental composition of the samples was measured using PerkinElmer ICP mass spectrometer, NexION™ 350X Model (PerkinElmer Company, Waltham, MA, USA). The equipment can identify and measure the concentration of metal ions with a wide dynamic range and high-level sensibility. The digestates of baryte tailings or extracts were diluted to 1% (100 times). With an ultra-purity level of 99.9%, argon was used as carrier gas and produced partially ionizing plasma that excites the ions in the water samples injected into the mass spectrometer. ICP-MS calibration was performed using standard solutions (0.1 ppm, 0.4 ppm, 0.6 ppm, and 1 ppm) (as recommended by the National Institute of Standards and Technology). The R^2 values obtained by the calibration curves (> 0.996) justified the accuracy of the calibration procedures. The concentration of various elements was compared using values obtained during the calibration, and the concentration of each element is presented in parts per million (ppm) or mg/L. The differences were less than 15%. In case of a higher concentration, the solution was diluted and re-analyzed to ensure accurate heavy metal quantification of the digestates (analyzed water samples). The limit of detection (LOD) and limit of quantification (LOQ) for each metal are presented in Table A5 (Appendix A).

6.2.3.2 Heavy Metal Toxic Unit (TU) of Mine Water

The toxic unit (TU) is the ratio of metals' calculated concentration to the severe-effect level (SEL) value in a liquid medium. TU presents potential acute toxicity limits for the contaminants in the media. Potential acute toxicity of the media occurs whenever the sum of the toxic units is greater than 4 (that means the toxicity of one or more metals in the media exceeds the recommended LEL). The sum of low-effect levels (LELs) for metals under consideration for this study is 4. Thus, the sum of toxicity values of metals in a medium cannot sufficiently pose/cause acute toxicity in humans if the value is less than 4 and each toxic unit is far below the lowest LEL (Bai et al., 2011; Daburum et al., 2019; JohnPaul et al., 2020; Laniyan & Adewumi, 2020a).

$$\mathrm{TU} = \frac{\text{Concentration of metal in media}}{\mathrm{SEL}} \tag{6.1}$$

Under a given condition, the SEL values for Zn, Cu, Fe, Pb, and Cd are shown in Table 6.1 (Agency, 2006; Bai et al., 2011; U. S. EPA, 2004; EU-OSHA, 2009; JohnPaul et al., 2020; Laniyan & Adewumi, 2020a).

Table 6.1: SEL and TU of heavy metals in the environment.

Heavy Metals	Severe-Effect Level (SEL)	TU (mg/L)	Standards
Zn	820	3.0–5.0	EU, NIS, US EPA [45,62,70]
Cd	10	0.001–0.005	EU, NIS, US EPA [53,64–66,69]
Cu	110	1.3–3.0	EU, NIS, US EPA [45,71]
Ba	Not yet reported	0.7–4.0	EU, NIS, US EPA [46]
Fe	4	0.3	EU, NIS, US EPA [46,62,71]
Pb	250	0.005–0.01	EU, NIS, US EPA [62,71,72]

EU: European Union, NIS: Nigerian Industrial Standard, US EPA: United States Environmental Protection Agency. [45,46,53,62,64-66,69-72]= (A. J. P. Adewumi & Laniyan, 2020; Aladesanmi, 2018; Bai et al., 2011; U. EPA, 2016; JohnPaul et al., 2020; Melekestseva et al., 2014; NIS-554-2015, 2015)

The SEL value for Ba was not available in the literature, as shown in Table 6.1. However, the TU for Ba compounds, soluble and insoluble, is reported and found to be between TUs for Cu and Fe. Thus, the linear interpolation formula used TUs and SELs for Cu and Fe to obtain an approximate SEL value for Ba by applying. The SEL value of 64.6 was calculated using Equation (2) and used in this study based on the SEL values of Cu and Fe.

Equation (6.2) is obtained by substituting the dependent variables and variables at different points, where Ba (independent variable), Fe (1), and Cu (2), respectively.

$$\mathrm{SEL_{Ba}} = \frac{(\mathrm{MAL_{Ba}} - \mathrm{MAL_{Fe}})(\mathrm{SEL_{Cu}} - \mathrm{SEL_{Fe}})}{(\mathrm{MAL_{Cu}} - \mathrm{MAL_{Fe}})} + \mathrm{SEL_{Fe}} \qquad (6.2)$$

where:

$\mathrm{SEL_{Ba}}$: SEL for barium

$\mathrm{SEL_{Cu}}$: SEL for copper

$\mathrm{SEL_{Fe}}$: SEL for iron

$\mathrm{MAL_{Ba}}$: maximum allowable limit for barium

$\mathrm{MAL_{Cu}}$: maximum allowable limit for copper

$\mathrm{MAL_{Fe}}$: maximum allowable limit for iron

6.2.4. Quantitative Risk Analysis and Calculation

6.2.4.1. Contamination Assessment

This describes the extent to which Ba, Fe, Zn, Pb, Cu, and Cd contaminate water in the ponds, rivers, and other water used for different activities by the artisanal miners and mining communities.

6.2.4.1.1 Geo-Accumulation Index (Igeo)

Muller (1969) calculated and classified the geo-accumulation index (Igeo) using Equation (6.3) (Muller, 1969).

$$Igeo = log_2 \frac{C_n}{1.5 \times B_n} \quad (6.3)$$

C_n is the concentration of metal in water samples (mg/L or ppm), and B_n is the metal concentration in water before the introduction of metals due to mining activities (mg/L or ppm). The constant value of 1.5 is a correction factor introduced into the equation to minimize the degree of deviation in the background values due to the lithologic variations in the water. Thus, the sample is unpolluted when Igeo < 0; unpolluted to moderately polluted (0 ≤ Igeo < 1); moderately polluted (1 ≤ Igeo < 2); moderately to severely polluted (2 ≤ Igeo < 3); severely polluted (3 ≤ Igeo <4); severely to enormously polluted (4 ≤ Igeo < 5); and enormously polluted (Igeo ≥ 5).

6.2.4.1.2 Contamination Factor (CF)

The contamination factor (CF) is a single-element index and classifies water contamination according to the work of Hakanson (1980). The contamination is low for CF < 1; moderately contaminated for 1≤ CF < 3; significantly contaminated for 3 ≤ CF < 6; and very high contamination for CF ≥ 6. The expression for CF is given in Equation (6.4). In this study, the CF for all elements in the tailing effluents is defined as the CF of the mining environment. This is limited to water samples from barite ponds and tailings within the three artisanal baryte mining sites under study (Muller, 1969).

$$\mathrm{CF} = \frac{\mathrm{CM}}{\mathrm{CB}} \quad (6.4)$$

CF is the contamination factor (dimensionless/unitless), CM is the mean metal concentration (mg/L), and CB is the concentration of elements in the background sample (mg/L).

6.2.4.2 Health Risk Assessment and Chronic Daily Intake (CDI)

Metals transported by water or dispersed as sediments in the water get into the human body through the oral and dermal pathways. Muhammad et al. (2011) defined oral ingestion through drinking water as the chronic daily intake (CDI), which is given in Equation (6.5) (Hakanson, 1980; Muhammad et al., 2011). The CDI expresses the degree of toxicity of heavy metals and presents the risk level. In risk assessment, CDIs are compared to the maximum tolerable daily intake (MTDI). The daily intake is described as chronic when the daily dose exceeds MTDI (CDI > MTDI). CDI varies as a function of mean heavy metal concentration in water, dose intake, and body weight:

$$CDI\left(\frac{\mu g}{kg\ day}\right) = \frac{C_{MW} \times IR}{BW} \tag{6.5}$$

C_{MW} is the concentration of heavy metals in water (mg/L), and BW and IR are the body weight (kg) and daily water ingestion rate (mg/day), respectively. These values are taken from Tables A1–A3 in Appendix A (Agency, 2006; Brenniman et al., 1979; U. S. EPA, 2004; Gholami et al., 2020; NIS-554-2015, 2015; Shah et al., 2016; Standardization, 2007; WHO, 2004).

2.4.3. Exposure Assessment

US EPA (2016) and Adewumi and Laniyan (2020) calculated the average annual exposure to heavy metals in water samples due to oral ingestion (EXP_{ing}) and dermal (skin) exposure (EXP_{dem}) using Equations (6.6) and (6.7), respectively.

$$EXP_{ing} = \frac{CM_0 \times I_R \times E_F \times E_D}{B_W \times AT} \tag{6.6}$$

$$EXP_{derm} = \frac{CM_0 \times I_R \times E_F \times E_D \times S_A \times P_C \times CF}{B_W \times AT} \tag{6.7}$$

$sEXP_{ing}$ and EXP_{derm} are the exposure dose rate through ingestion (mg $kg^{-1}d^{-1}$) and diffusion through the skin (dermal pathway) (mg $kg^{-1}d^{-1}$); CM_0: concentration of heavy metals in the sample (mg/L); I_R: ingestion rate (mg/day); E_F: exposure frequency (days/year); E_D: exposure duration (years); B_W: body weight (kg); AT: average time (days); S_A: skin surface area (cm^2); P_C: dermal permeability coefficient; CF: conversion factor (kg/mg). Exposure dose rate via ingestion and diffusion along the skin can vary with the concentration of the heavy metals, their solubility in tissue fluids, amount of blood circulation, the toxicity of the metals, exposure duration, and time. A small concentration of toxic chemicals such as Pb can cause severe damage to the body over a long time. These exposure indices are computed using values presented in Tables A1–A3 (A. J. Adewumi & Laniyan, 2020; U. S. EPA, 2004; U.S. Environmental Protection Agency, 2016).

6.2.5. Risk Characterization

6.2.5.1. Hazard Quotient (HQ)

HQ is defined as a single-element hazard quotient and quantifies a single-element risk. In the case of two or more heavy metals, the multi-elemental risk assessment is performed using the hazard index, as presented in Equation (6.8) (U. S. EPA, 2004; Nazaroff & Alvarez-Cohen, 2001b; U.S. Environmental Protection Agency, 2016).

$$\mathrm{HQ} = \frac{CDI_{non\ carcinogenic}}{\mathrm{RfD}} \qquad (6.8)$$

For non-carcinogenic elements, the risk is defined as the hazard quotient (HQ). HQ is the hazard quotient and measures the amount or percentage propensity to hazard caused by the ingestion of metals or exposure through the dermal pathway for non-carcinogenic substances. $CDI_{non\ carcinogenic}$: chronic daily intake for non-carcinogenic heavy metals such as Ba, Zn, Cu, and Fe. In addition, RfD is the reference dose factor and the no-observable-adverse-effect level (NOAEL) over the uncertainty factor (UF). The reference dose (RfD) and uncertainty factor (UF) for each heavy metal are used to estimate the intake rate of toxic metals via oral and dermal pathways for the non-carcinogenic effect. Based on RfD and UF, the risk threshold and associated damages are identified as chronic doses accumulated. Exposure to heavy metals above an acceptable threshold of 10^{-6} (1 part per million) (LOAEL) results in a lifetime risk called individual excess lifetime cancer risk (IELCR). However, there is undoubtedly no threshold for carcinogenic risk because the effect of the episodic doses accumulates whenever the exposure is sure. Thus, NOAEL and LOAEL hold that an individual excess lifetime or very low cancer risk (IELCR) exist for carcinogenic effect (risk level 1) while risk levels for the non-carcinogenic effect are defined using scale 1–4 (no risk to high risk) (G. M. EPA, 1999; Nazaroff & Alvarez-Cohen, 2001a; Rapant et al., 2011; Shah et al., 2016).

Nazaroff and Alvarez-Cohen (2001) and US EPA (2016) established that water is probably safe and no longer harmful to human health when HQ is far below the lowest-observable-adverse-effect level (LOAEL) or <1 (where LOAEL is unity). However, it is regarded as toxic, unsafe, and may initiate chronic disease when HQ is above the LOAEL or HQ > 1. Similarly, RAIS (2020) and Rapant et al. (2010) classified non-carcinogenic risks as "negligible chronic risk (HQ < 0.1), low risk (0.1 < HQ < 1), medium risk (1 < HQ < 4), and high risk (HQ > 4)" (G. M. EPA, 1999; Rapant et al., 2011).

RAIS (2020) and EPA (1989) calculated the non-carcinogenic risk as to the ratio of the hazard quotient to the hazard index (HQ/HI). When (HQ/HI) < 0.1, safety is guaranteed, or an adverse health effect is not likely (A. B. D. EPA, 1989; Nazaroff & Alvarez-Cohen, 2001a). There is an adverse non-carcinogenic risk to human health when (HQ/HI) = 1. At the same time, the 0.1 < (HQ/HI) < 1 indicates that some precautionary measures should be taken to avert potential danger or mining hazards.

6.2.5.2. Maximally Exposed Individual (MEI)

Maximally exposed individual (MEI) assesses the risk to the health and well-being of the mining community (residents) and miners. The harm caused by non-carcinogenic substances such as Ba, Cu, Zn, and Fe was examined and compared to values at the threshold below which the human body can manage the risk or recover before subsequent exposure (Nazaroff & Alvarez-Cohen, 2001a; Shah et al., 2016). MEI was computed using Equation (6.9).

$$\mathrm{MEI} = \mathrm{C}\frac{\mathrm{CR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \tag{6.9}$$

MEI is maximally exposed individual (mg $kg^{-1}d^{-1}$); C is the average concentration of a contaminant at exposure (mg/L in water samples); CR: contact rate (L/day); EF: exposure frequency (days/year); ED: exposure duration (years); BW: body weight (kg); and AT: period over (days) which exposure is typical.

6.3 Results

6.3.1. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) Analysis

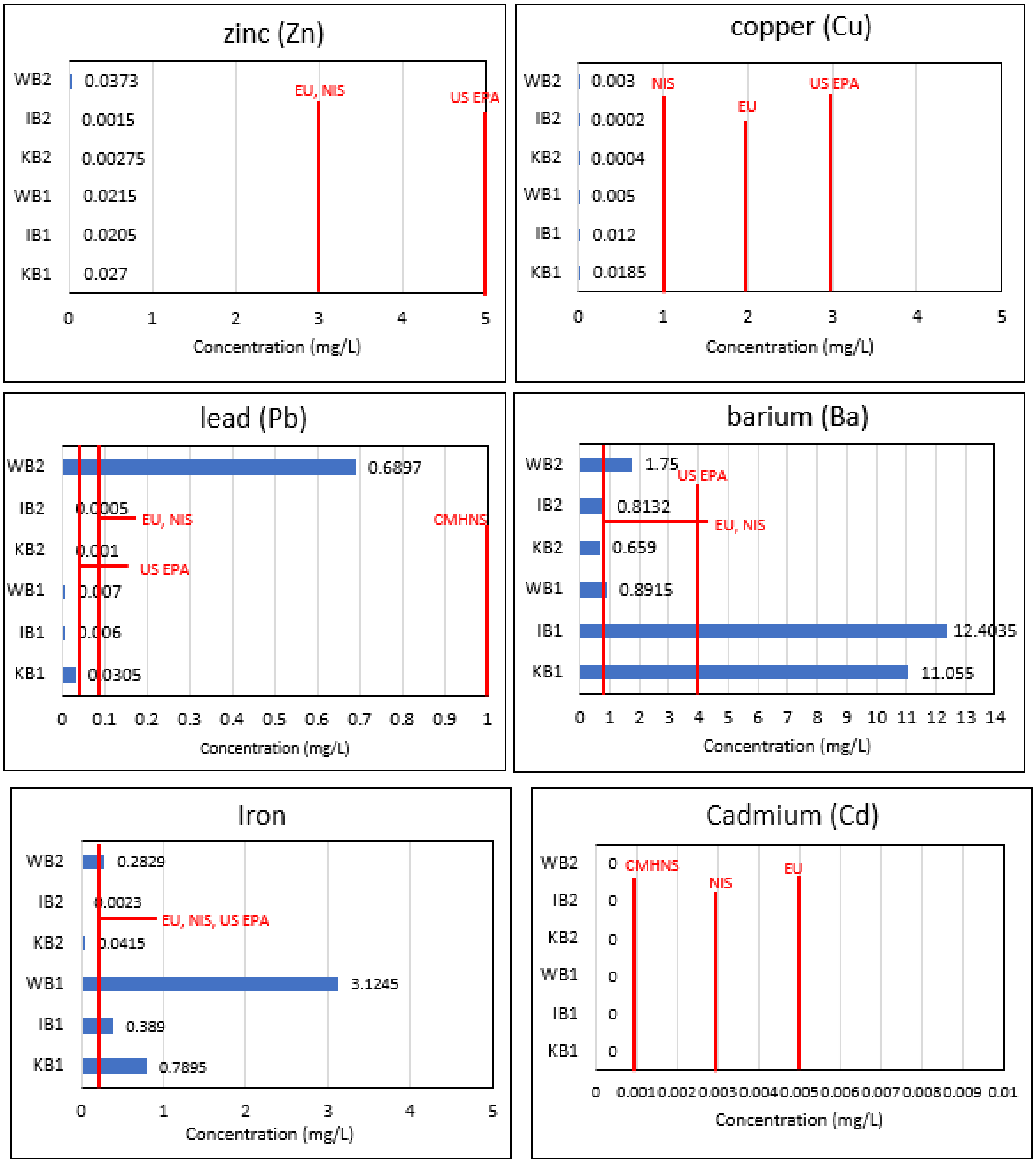
The ICP-MS analysis in Figure 6.3 identifies Zn, Cu, Ba, Cd, Fe, and Pb metal ions in the mine tailings in different quantities. In this study, the metal concentrations in mine tailings decrease in the order of Ba > Fe > Pb > Zn > Cu > Cd. The concentration of each metal ion in all the samples was compared with the global ecological, environmental, and health standards. Zn, Cu, and Cd are below the maximum allowable limit set by WHO, EU, NIS, US EPA, and CMHNS for ecological and health safety. However, the content of Ba in KB1 and IB1 and Fe in KB1, IB1, and WB1 is relatively higher than the maximum allowable limits set by the governing standards, as shown in Table A4. Similarly, Pb in WB2 is above the health and environmental risk levels recommended by the local and international agencies. This outcome indicates that the water used in the ore washing will result in water pollution and heavy metal ingestion if returned to rivers and streams used by people.

Medical research reports on the human intake of Fe by the NIS (2015) and DNR (2017) show that Fe in water has no identifiable damage or adverse effect on human health when the concentration is below 45 mg/day in men (tolerable upper intake level in an adult only). The maximum concentration of Fe obtained in WB1 mine tailing was 3.1245 mg/L. This was followed by KB2 (0.7895 mg/L) and IB1 (0.389 mg/L). The concentration of Fe in KB2, IB2, and WB2 was found to be between 0.003 and 0.2829 mg/L. However, the day-to-day consumption of iron in the water contaminated by baryte mine tailings could be greater than the value reported in this study. Research has also shown that Fe in surface water at an artisanal gold mine in Nigeria during the wet season can be higher than the value reported in this study (A. J. Adewumi & Laniyan, 2020; A. J. P. Adewumi et al., 2020; Adeniyi JohnPaul Adewumi & Laniyan, 2021). Water with high Fe can have a sense of taste, subject to microbial attack by Fe utilization, and be coloured. Thus, water quality is compromised, becomes prone to biocides, and makes the water treatment process unrealizable (NIS-554-2015, 2015). The taste of the mine water was not examined during the survey. However, the water samples are brownish-red.

Several research studies have shown that Ba in drinking water may be responsible for dental caries in children, cardiovascular and heart diseases, nephropathy in laboratory animals, and a potential cause of high blood pressure in humans, as reported by WHO (2004) (Brenniman et al., 1979; Brenniman & Levy, 1984; WHO, 2004; Zdanowicz et al., 1987). Ba is considered non-carcinogenic in humans and animals (animal trials on mice) (Brenniman et al., 1979; DNR, 2017; WHO, 2004). However, an acute oral dose is between 3 and 4 g/day in humans. In the current study, the concentration of Ba in mine tailing digestate IB1 is 12.40 mg/L, followed by 11.06 mg/L in digestate KB1, as shown in Figure 6.3. The lower concentration of Ba observed was between 0.66 and 1.75 mg/L in KB2, IB2, WB1, and WB2 digestates. These values are higher than the maximum allowable limit values (as shown in Figure 6.3).

Pb is toxic for humans, plants, and animals. It is also the primary cause of kidney malfunction and serious hematologic and brain damage in mammals (Tokalıoğlu et al., 2018; Zdanowicz et al., 1987). Pb levels are found to be above the maximum permissible values indicated by WHO, EU, and NIS in WB2 (0.69 mg/L) and KB1 (0.03 mg/L), as shown in Table 6A4. The lowest Pb levels were between 0.0005 mg/L and 0.007 mg/L in WB1, IB1, KB2, and IB2. The allowable limit for Pb is 0.01 mg/L (EU, NIS, Nigerian Standard for Drinking Water Quality, and CHMNS standards) and 0.005 (US EPA standard). Pb concentration in tailing digestates WB2 and KB1 exceeds the drinking water limit.

Zn, Cu, and Cd concentrations in the digestate of the mine tailings are in all cases below the maximum allowable limits; in particular, Cd has an undetectable concentration. The highest concentration for copper is 0.019 mg/L in KB1. Digestates of KB1, IB1, WB1, KB2, IB2, and WB2 have Zn concentrations in the range of 0.003 mg/L and 0.04 mg/L. Similarly, the average Cu concentration in the digestates was ≤ 0.01 mg/L. The concentrations of zinc and copper in all the digestates were lower than the allowable limits recommended by the standards. This implies that zinc and copper toxicities of the tailings' digestates cannot be responsible for irritability and muscular stiffness in humans (Zdanowicz et al., 1987). As reported in the literature, Zn and Cu concentrations may be low and high in soil and water around barite mining sites and gold mining sites (Ishaya, 2019; Obasi & Akudinobi, 2020; I Ochelebe et al., 2020). Thus, the zinc and copper concentrations vary across baryte mining sites but are lower than those in gold and Pb-Zn mining sites.



WHO: World Health Organization; EU: European Union; NIS: Nigerian Industrial Standard; USEPA: United States Environmental Protection Agency; CMHNS: China Ministry of Health National Standards

Figure 6.3: Concentration of heavy metals associated with artisanal baryte mining (ABM) at some mining sites within the Middle Benue Trough, Nigeria.

6.3.2 Heavy Metal Toxic Unit (TU) Results

Table 6.2 shows that the heavy metal toxicity is of the order Cd < Zn < Cu < Pb < Ba < Fe. The contributions of Fe (79.75%) and Ba (19.60%) dominate the toxicity index. Zn, Cu, and Pb contributed 0.010%, 0.017%, and 0.62%, respectively, to the total toxic unit (TTU) of pollutants associated with barite mining. There is a clear indication that barite mining activities are free of cadmium toxicity. Moreover, the total TU in the media is 0.9797, which is far less than 4 (toxicity of each element is less than the SEL), indicating low toxicity or low chronic risk level. The sum of low-effect levels (LELs) for metals under consideration for this study is 4, which agrees with the scale used to characterize the chronic risk level as stipulated by the United States Environmental Protection Agency (US EPA). Scales 1–4 are standardized scales used to characterize chronic risk levels. Scale 4 is defined as a high chronic risk level. Potential acute toxicity of the media occurs whenever the sum of the toxic units is greater than 4 (that means the toxicity of one or more metals in the media exceeds the recommended low-effect level (LEL)) (A. J. P. Adewumi & Laniyan, 2020; JohnPaul et al., 2020; Vandi et al., 2019). The toxic level (TU) of the media increases in the order of IB2 < KB2 < WB2 < IB1 < KB1 < WB1. However, it was reported that the toxic level of heavy metals in sediments and soil is higher than in mine water or water contaminated by heavy metals from the field sites. The continuous release and subsequent accumulation of these toxic metals into the ecosystem may increase the TUs and result in numerous ecological and health risks if the exploitation process remains unchecked.

Table 6.2: Toxic units and contamination factor (CF) of identified heavy metals associated with some baryte mines in Nigeria.

Heavy Metals	Maximum Metallic Conc in Media (ppm)	SEL	Toxic Unit (TU)	% TU
Zinc	0.0805	820	0.0000975	0.010
Copper	0.0185	110	0.000168	0.017
Iron	3.1245	4	0.78135	79.750
Lead	1.516	250	0.0061	0.62
Cadmium	0.000	10	0.000	0.00

Barium	12.4035	64.6	0.192	19.6
			∑= 0.9797.	

6.3.3 Hazard/Risk Assessment of Water contaminated by Tailing Effluents and Baryte Ponds

6.3.3.1 Geo-accumulation Index (Igeo)

Figure 6.4 shows that in all cases analyzed, Zn and Cu concentrations at abandoned barite mining sites do not pollute water resources (Igeo < 0). Pb, Fe, and Ba concentrations at some sites have Igeo values greater than zero, indicating that the barite tailings and ponds are moderately-severely polluted (Pb and Ba in KB1, Ba in IB1, and Fe in WB1—Igeo = 2–3) to enormously polluted (Pb in WB2—Igeo > 5). Cu has Igeo < 0, and thus its concentration does not pollute the water.

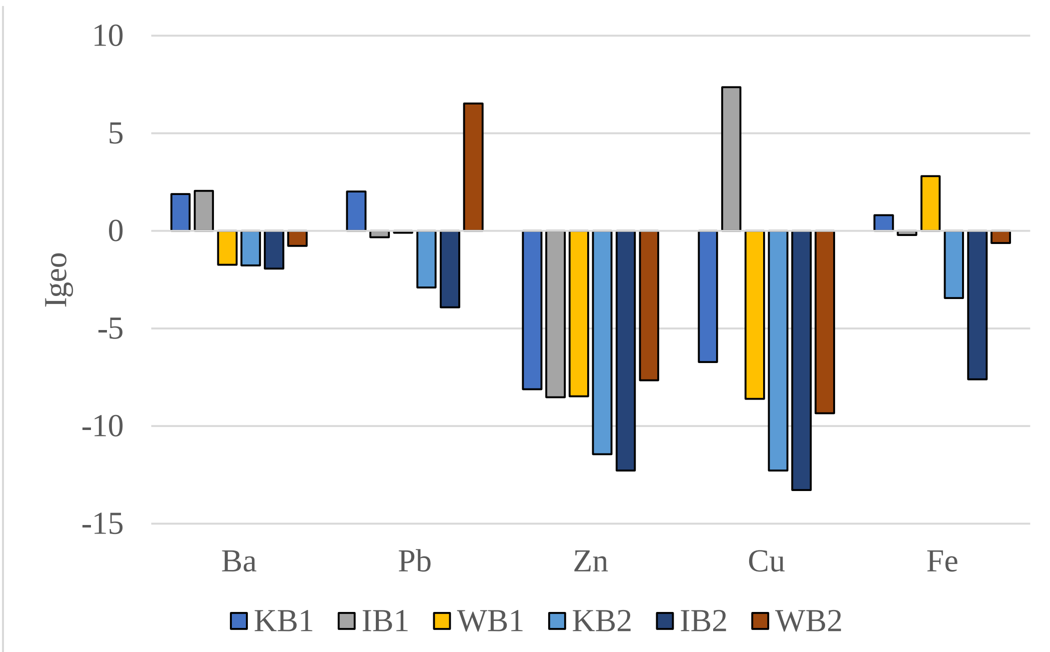


Figure 6.4: Geo-accumulation index (Igeo) for the water samples.

6.3.3.2. Contamination Factor (CF)

Table 6.3 shows that Zn and Cu have a very low CF (<0.02) in all analyzed sites. Site KB2 was low in contamination as it had a CF < 1 for all metals analyzed. Pb, Fe, and Ba have CF values greater than zero, indicating that the barite ponds and water resources are moderately contaminated (Pb in IB1 and WB1 and Fe in KB1 and IB1) to highly contaminated (Pb in KB1, Ba in KB1 and IB1, and Fe in WB1). The contamination assessment studies based on Igeo and CF showed that some of the mine water is moderately to severely polluted by Ba and Fe, extremely polluted by Pb, and very highly contaminated by Ba, Pb, and Fe.

Table 6.3: Contamination factor (CF) of heavy metals in mine water and tailing effluents.

Elements	Ba	Pb	Zn	Cu	Fe
(CF) (dimensionless)					
KB1	5.528	6.100	5.4×10^{-3}	1.4×10^{-2}	2.630
IB1	6.202	1.200	4.1×10^{-3}	3.8×10^{-3}	1.297
WB1	0.446	1.400	4.3×10^{-3}	3.0×10^{-4}	10.415
KB2	0.330	0.200	5.5×10^{-4}	7.7×10^{-4}	0.138
IB2	0.407	0.100	3.0×10^{-4}	-------	0.008
WB2	0.875	137.940	7.46×10^{-3}	2.3×10^{-3}	0.943

6.3.4 Health Risk Assessment

6.3.4.1 Chronic Daily Intake (CDI)

Table 6.4 shows that the CDI for Ba, Pb, Zn, Fe, and Cu in baryte ponds or mine water and tailing effluents is between 2.35×10^{-6} mg/kg day (for Cu in IB2) and 1.46×10^{-1} mg/kg day (for Ba in IB1) for an adult and between 2.19×10^{-6} mg/kg day (for Cu in IB2) and 1.36×10^{-1} mg/kg day (for Ba in IB1) for children. These concentrations indicate the lifetime average daily dose. The result presents the possible consequence of long-term exposure to heavy metals—accumulation through ingestion and dermal pathway that can initiate chronic diseases in humans over a long period. The heavy metals' concentration at barite mining sites for Pb was higher than those reported for cosmetics (Pb at 0.02885 mg kg^{-1} d^{-1}) (Oluwatuyi et al., 2020b) and is within the range reported for Pb, Zn, Cu, and Fe on artisanal gold mining sites (A. J. P. Adewumi & Laniyan, 2020; Alam et al., 2019).

6.3.4.2. Maximally Exposed Individual (MEI)

In Table 6.4, Ba shows the highest values (for residents and workers) in KB1, IB1, and WB1. Pb, Fe, and Zn show higher values for residents than workers for KB1, IB1, KB1, and WB2. Exposure levels for Zn, Cu, and Fe are low for residents and workers at the mining sites and may not pose any health risk. Miners who reside outside the mining community consume 5.20×10^{-1}

mg kg^{-1} d^{-1} of Ba, 1.48 × 10^{-2} mg kg^{-1} d^{-1} of Pb, 6.75 × 10^{-3} mg kg^{-1} d^{-1} of Zn, 1.18 × 10^{-4} mg kg^{-1} d^{-1} of Cu, and 3.06 × 10^{-2} mg kg^{-1} d^{-1} of Fe.

Table 6.4: Chronic daily intake (CDI) and maximally exposed individual (MEI) to heavy metals in mine water and tailing effluents.

Samples	Ba	Pb	Zn	Cu	Fe
(CDI) Adult (mg kg^{-1} d^{-1})					
KB1	$\mathbf{1.29 \times 10^{-1}}$	$\mathbf{3.58 \times 10^{-4}}$	$\mathbf{3.17 \times 10^{-4}}$	$\mathbf{2.17 \times 10^{-4}}$	$\mathbf{9.27 \times 10^{-3}}$
IB1	$\mathbf{1.46 \times 10^{-1}}$	$\mathbf{7.05 \times 10^{-5}}$	$\mathbf{2.41 \times 10^{-4}}$	$\mathbf{1.41 \times 10^{-4}}$	$\mathbf{4.56 \times 10^{-3}}$
WB1	$\mathbf{1.05 \times 10^{-2}}$	$\mathbf{8.21 \times 10^{-5}}$	$\mathbf{2.52 \times 10^{-4}}$	$\mathbf{5.87 \times 10^{-5}}$	$\mathbf{3.67 \times 10^{-2}}$
KB2	$\mathbf{7.70 \times 10^{-3}}$	$\mathbf{1.17 \times 10^{-5}}$	$\mathbf{3.22 \times 10^{-5}}$	$\mathbf{4.70 \times 10^{-6}}$	$\mathbf{4.87 \times 10^{-4}}$
IB2	$\mathbf{9.50 \times 10^{-3}}$	$\mathbf{5.87 \times 10^{-6}}$	$\mathbf{1.76 \times 10^{-5}}$	$\mathbf{2.35 \times 10^{-6}}$	$\mathbf{2.70 \times 10^{-5}}$
WB2	$\mathbf{2.05 \times 10^{-2}}$	$\mathbf{8.09 \times 10^{-3}}$	$\mathbf{4.38 \times 10^{-4}}$	$\mathbf{3.52 \times 10^{-5}}$	$\mathbf{3.32 \times 10^{-3}}$
(CDI) Child (mg kg^{-1} d^{-1})					
KB1	$\mathbf{1.21 \times 10^{-1}}$	$\mathbf{3.34 \times 10^{-4}}$	$\mathbf{2.95 \times 10^{-4}}$	$\mathbf{2.03 \times 10^{-4}}$	$\mathbf{8.65 \times 10^{-3}}$
IB1	$\mathbf{1.36 \times 10^{-1}}$	$\mathbf{6.57 \times 10^{-5}}$	$\mathbf{224 \times 10^{-4}}$	$\mathbf{1.32 \times 10^{-4}}$	$\mathbf{4.26 \times 10^{-3}}$
WB1	$\mathbf{9.70 \times 10^{-3}}$	$\mathbf{6.67 \times 10^{-5}}$	$\mathbf{2.35 \times 10^{-4}}$	$\mathbf{5.48 \times 10^{-5}}$	$\mathbf{3.42 \times 10^{-2}}$
KB2	$\mathbf{7.20 \times 10^{-3}}$	$\mathbf{1.10 \times 10^{-5}}$	$\mathbf{3.01 \times 10^{-5}}$	$\mathbf{4.38 \times 10^{-6}}$	$\mathbf{4.54 \times 10^{-4}}$
IB2	$\mathbf{8.90 \times 10^{-3}}$	$\mathbf{5.47 \times 10^{-6}}$	$\mathbf{1.64 \times 10^{-5}}$	$\mathbf{2.19 \times 10^{-6}}$	$\mathbf{2.52 \times 10^{-5}}$
WB2	$\mathbf{1.92 \times 10^{-2}}$	$\mathbf{7.56 \times 10^{-3}}$	$\mathbf{4.09 \times 10^{-4}}$	$\mathbf{3.29 \times 10^{-5}}$	$\mathbf{3.10 \times 10^{-3}}$
(MEI) Resident (mg kg^{-1} d^{-1})					
KB1	$\mathbf{3.03 \times 10^{-1}}$	$\mathbf{8.36 \times 10^{-4}}$	$\mathbf{7.40 \times 10^{-4}}$	$\mathbf{5.07 \times 10^{-4}}$	$\mathbf{2.16 \times 10^{-2}}$
IB1	$\mathbf{3.40 \times 10^{-1}}$	$\mathbf{1.64 \times 10^{-4}}$	$\mathbf{5.61 \times 10^{-4}}$	$\mathbf{3.29 \times 10^{-4}}$	$\mathbf{1.07 \times 10^{-2}}$
WB1	$\mathbf{5.20 \times 10^{-1}}$	$\mathbf{1.92 \times 10^{-4}}$	$\mathbf{5.89 \times 10^{-4}}$	$\mathbf{1.37 \times 10^{-4}}$	$\mathbf{8.56 \times 10^{-2}}$
KB2	$\mathbf{1.81 \times 10^{-3}}$	$\mathbf{2.74 \times 10^{-5}}$	$\mathbf{7.53 \times 10^{-5}}$	$\mathbf{1.10 \times 10^{-5}}$	$\mathbf{1.13 \times 10^{-3}}$
IB2	$\mathbf{2.22 \times 10^{-2}}$	$\mathbf{1.37 \times 10^{-5}}$	$\mathbf{4.11 \times 10^{-5}}$	$\mathbf{5.48 \times 10^{-6}}$	$\mathbf{6.30 \times 10^{-5}}$
WB2	$\mathbf{4.79 \times 10^{-2}}$	$\mathbf{1.89 \times 10^{-2}}$	$\mathbf{1.89 \times 10^{-2}}$	$\mathbf{8.22 \times 10^{-5}}$	$\mathbf{7.75 \times 10^{-3}}$
(MEI) Worker (mg kg^{-1} d^{-1})					
KB1	$\mathbf{1.08 \times 10^{-1}}$	$\mathbf{2.99 \times 10^{-4}}$	$\mathbf{2.64 \times 10^{-4}}$	$\mathbf{1.81 \times 10^{-4}}$	$\mathbf{7.71 \times 10^{-3}}$
IB1	$\mathbf{1.21 \times 10^{-1}}$	$\mathbf{1.64 \times 10^{-4}}$	$\mathbf{2.00 \times 10^{-4}}$	$\mathbf{1.18 \times 10^{-4}}$	$\mathbf{3.82 \times 10^{-3}}$
WB1	$\mathbf{1.86 \times 10^{-1}}$	$\mathbf{5.86 \times 10^{-5}}$	$\mathbf{2.10 \times 10^{-4}}$	$\mathbf{4.89 \times 10^{-5}}$	$\mathbf{3.06 \times 10^{-2}}$
KB2	$\mathbf{7.43 \times 10^{-3}}$	$\mathbf{9.79 \times 10^{-6}}$	$\mathbf{2.69 \times 10^{-5}}$	$\mathbf{3.92 \times 10^{-6}}$	$\mathbf{4.04 \times 10^{-4}}$
IB2	$\mathbf{7.93 \times 10^{-3}}$	$\mathbf{4.89 \times 10^{-6}}$	$\mathbf{1.47 \times 10^{-5}}$	$\mathbf{1.96 \times 10^{-6}}$	$\mathbf{2.25 \times 10^{-5}}$
WB2	$\mathbf{1.71 \times 10^{-2}}$	$\mathbf{6.75 \times 10^{-3}}$	$\mathbf{6.75 \times 10^{-3}}$	$\mathbf{2.94 \times 10^{-5}}$	$\mathbf{2.77 \times 10^{-3}}$

6.3.5. Hazard Exposure Assessment

Risks due to heavy metal contamination are difficult to quantify, but it is important to identify the sources of hazard and the exposure level to humans.

The results (Table 6.5) show that oral ingestion (EXP_{ing}) is between 1.03×10^{-1} and 1.399×10^{1} mg kg^{-1}d^{-1} for Ba, 5.48×10^{-4} and 1.78 mg kg^{-1} d^{-1} for Pb, 8.80×10^{-4} and 8.82×10^{-2} mg kg^{-1} d^{-1} for Zn, 1.17×10^{-4} and 2.02×10^{-2} mg kg^{-1} d^{-1} for Cu, and 1.35×10^{-3} and 3.42 mg^{2} L^{-1} kg^{-1} d^{-1} for Fe, respectively. Similarly, the values of EXP_{derm} are between 4.55×10^{-5} and 1.27×10^{-3} mg kg^{-1} d^{-1} for Ba, 4.60×10^{-9} and 2.06×10^{-5} mg kg^{-1} d^{-1} for Pb, 2.07×10^{-8} and 1.64×10^{-6} mg kg^{-1} d^{-1} for Zn, 4.60×10^{-9} and 4.26×10^{-7} mg kg^{-1} d^{-1} for Cu, and 5.29×10^{-8} and 1.06×10^{-4} mg kg^{-1} d^{-1} for Fe, respectively. Ba, Pb, and Fe show the highest values for EXP_{ing}, while Cu has the lowest value for EXP_{ing}. Similarly, Ba also shows the highest value for EXP_{derm}. The miners and people living within the mining sites are more exposed to associated health hazards through ingestion than a dermal pathway. Similarly, results also show that the estimated health risks of heavy metals per kilogram of children's body weight are higher than adults.

Table 6.5. Exposure assessment (EXP) of heavy metals in mine water and tailing effluents through ingestion (EXP_{ing}) and skin (dermal pathways (EXP_{derm})).

Elements	Ba	Pb	Zn	Cu	Fe
EXP_{ing} (mg kg^{-1} d^{-1}) Adult					
KB1	$\mathbf{6.49 \times 10^{0}}$	$\mathbf{1.79 \times 10^{-2}}$	$\mathbf{1.59 \times 10^{-2}}$	$\mathbf{1.09 \times 10^{-2}}$	$\mathbf{4.60 \times 10^{-1}}$
IB1	$\mathbf{7.28 \times 10^{0}}$	$\mathbf{3.52 \times 10^{-3}}$	$\mathbf{1.20 \times 10^{-2}}$	$\mathbf{7.05 \times 10^{-3}}$	$\mathbf{2.23 \times 10^{-1}}$
WB1	$\mathbf{5.20 \times 10^{-1}}$	$\mathbf{4.11 \times 10^{-3}}$	$\mathbf{1.26 \times 10^{-2}}$	$\mathbf{2.94 \times 10^{-3}}$	$\mathbf{1.83 \times 10^{0}}$
KB2	$\mathbf{3.86 \times 10^{-1}}$	$\mathbf{5.87 \times 10^{-4}}$	$\mathbf{1.61 \times 10^{-3}}$	$\mathbf{2.34 \times 10^{-4}}$	$\mathbf{2.43 \times 10^{-2}}$
IB2	$\mathbf{4.77 \times 10^{-1}}$	$\mathbf{2.94 \times 10^{-4}}$	$\mathbf{8.80 \times 10^{-4}}$	$\mathbf{1.17 \times 10^{-4}}$	$\mathbf{1.35 \times 10^{-3}}$
WB2	$\mathbf{1.03 \times 10^{-1}}$	$\mathbf{4.05 \times 10^{-1}}$	$\mathbf{2.19 \times 10^{-2}}$	$\mathbf{1.76 \times 10^{-3}}$	$\mathbf{1.66 \times 10^{-1}}$
EXP_{ing} (mg L^{-1} kg^{-1} d^{-1}) Child					
KB1	$\mathbf{12.11 \times 10^{0}}$	$\mathbf{3.58 \times 10^{-2}}$	$\mathbf{2.96 \times 10^{-2}}$	$\mathbf{2.02 \times 10^{-2}}$	$\mathbf{8.65 \times 10^{-1}}$
IB1	$\mathbf{13.99 \times 10^{0}}$	$\mathbf{7.04 \times 10^{-3}}$	$\mathbf{2.24 \times 10^{-2}}$	$\mathbf{1.31 \times 10^{-2}}$	$\mathbf{4.26 \times 10^{-1}}$
WB1	$\mathbf{9.76 \times 10^{-1}}$	$\mathbf{8.22 \times 10^{-3}}$	$\mathbf{2.36 \times 10^{-2}}$	$\mathbf{5.48 \times 10^{-3}}$	$\mathbf{3.42 \times 10^{0}}$
KB2	$\mathbf{7.22 \times 10^{-1}}$	$\mathbf{1.17 \times 10^{-3}}$	$\mathbf{3.02 \times 10^{-3}}$	$\mathbf{4.38 \times 10^{-4}}$	$\mathbf{4.54 \times 10^{-2}}$
IB2	$\mathbf{8.92 \times 10^{-1}}$	$\mathbf{5.48 \times 10^{-4}}$	$\mathbf{1.64 \times 10^{-3}}$	$\mathbf{2.20 \times 10^{-4}}$	$\mathbf{2.52 \times 10^{-3}}$
WB2	$\mathbf{1.92 \times 10^{0}}$	$\mathbf{7.56 \times 10^{-1}}$	$\mathbf{4.08 \times 10^{-2}}$	$\mathbf{3.28 \times 10^{-4}}$	$\mathbf{3.10 \times 10^{-1}}$
EXP_{derm} (mg kg^{-1} d^{-1}) Adult					
KB1	$\mathbf{1.12 \times 10^{-3}}$	$\mathbf{4.15 \times 10^{-7}}$	$\mathbf{5.52 \times 10^{-7}}$	$\mathbf{2.30 \times 10^{-7}}$	$\mathbf{2.69 \times 10^{-5}}$
IB1	$\mathbf{1.27 \times 10^{-3}}$	$\mathbf{8.17 \times 10^{-8}}$	$\mathbf{4.18 \times 10^{-7}}$	$\mathbf{4.09 \times 10^{-7}}$	$\mathbf{1.32 \times 10^{-5}}$
WB1	$\mathbf{9.11 \times 10^{-5}}$	$\mathbf{9.53 \times 10^{-8}}$	$\mathbf{4.39 \times 10^{-7}}$	$\mathbf{1.70 \times 10^{-7}}$	$\mathbf{1.06 \times 10^{-4}}$
KB2	$\mathbf{6.73 \times 10^{-5}}$	$\mathbf{1.36 \times 10^{-8}}$	$\mathbf{5.62 \times 10^{-8}}$	$\mathbf{1.36 \times 10^{-8}}$	$\mathbf{1.41 \times 10^{-6}}$
IB2	$\mathbf{8.31 \times 10^{-5}}$	$\mathbf{6.81 \times 10^{-9}}$	$\mathbf{3.06 \times 10^{-8}}$	$\mathbf{6.81 \times 10^{-9}}$	$\mathbf{7.83 \times 10^{-8}}$

WB2	$\mathbf{1.79 \times 10^{-4}}$	$\mathbf{9.39 \times 10^{-6}}$	$\mathbf{7.62 \times 10^{-7}}$	$\mathbf{1.02 \times 10^{-7}}$	$\mathbf{9.63 \times 10^{-6}}$
EXP_{derm} ($mg\ kg^{-1}\ d^{-1}$) Child					
KB1	$\mathbf{7.63 \times 10^{-4}}$	$\mathbf{2.81 \times 10^{-7}}$	$\mathbf{3.73 \times 10^{-7}}$	$\mathbf{4.26 \times 10^{-7}}$	$\mathbf{1.82 \times 10^{-5}}$
IB1	$\mathbf{8.56 \times 10^{-4}}$	$\mathbf{5.52 \times 10^{-8}}$	$\mathbf{2.83 \times 10^{-7}}$	$\mathbf{2.76 \times 10^{-7}}$	$\mathbf{8.95 \times 10^{-6}}$
WB1	$\mathbf{6.16 \times 10^{-5}}$	$\mathbf{6.44 \times 10^{-8}}$	$\mathbf{3.00 \times 10^{-7}}$	$\mathbf{1.15 \times 10^{-7}}$	$\mathbf{7.19 \times 10^{-5}}$
KB2	$\mathbf{4.55 \times 10^{-5}}$	$\mathbf{9.21 \times 10^{-9}}$	$\mathbf{3.08 \times 10^{-8}}$	$\mathbf{9.21 \times 10^{-9}}$	$\mathbf{9.55 \times 10^{-7}}$
IB2	$\mathbf{5.61 \times 10^{-5}}$	$\mathbf{4.60 \times 10^{-9}}$	$\mathbf{2.07 \times 10^{-8}}$	$\mathbf{4.60 \times 10^{-9}}$	$\mathbf{5.29 \times 10^{-8}}$
WB2	$\mathbf{1.21 \times 10^{-4}}$	$\mathbf{6.35 \times 10^{-6}}$	$\mathbf{5.15 \times 10^{-7}}$	$\mathbf{6.90 \times 10^{-8}}$	$\mathbf{6.51 \times 10^{-6}}$

6.3.6. Hazard Characterization

HQ (Table 6.6) for Ba in adults and children ranges between 1.03×10^{-1} and 1.94 in children and 1.11×10^{-1} and 2.08 in adults; 3.90×10^{-3} and 1.19×10^{1} in children and 4.20×10^{-3} and 1.27×10^{1} in adults for Pb; 5.48×10^{-4} and 1.36×10^{-2} in children and 1.08×10^{-3} and 1.46×10^{-2} in adults for Zn; 5.48×10^{-5} and 5.07×10^{-3} in children and 5.87×10^{-5} and 5.40×10^{-3} in adults for Cu; and 1.76×10^{-5} and 6.06×10^{-3} in children and 3.86×10^{-5} and 5.24×10^{-2} in adults for Fe. Ba and Pb show high values for HQ (in children and adults), while Cu and Fe show the lowest values for HQ. Similarly, the HQs of tailing effluents KB1 and IB1 for Ba and WB2 for Pb are between 1 and 6. HQs of Zn, Cu, and Fe for all water samples are less than 0.1 for the water samples WB1, KB2, and IB2. Such HQ is classified as negligible chronic risk (HQ $<$ 0.1) (Nazaroff & Alvarez-Cohen, 2001a; Rapant et al., 2011) and cannot lead to adverse health implications. This indicates that an adverse effect is quite low.

HI (Table 6.6) shows high values for WB2, KB1, and IB1 in adults and KB1, IB1, and WB2 in children. HI of 5.81×10^{1} (WB2 in adults), 2.14×10^{0} (KB1 in adults), 2.15×10^{0} (IB1 in adults), 1.98×10^{0} (KB1 in children), $2.00 \text{ x } 10^{0}$ (IB1 in children), and 5.69×10^{0} (WB2 in children) indicate elevated non-carcinogenic risks. Similar research on water sources contaminated by ores also reported HQ and HI $>$ 1 and may be higher than values obtained in this study (A. J. P. Adewumi & Laniyan, 2020; Obasi & Akudinobi, 2020; Rapant et al., 2011). For Ba, HQ/HI is 0.97 (considering IB1 for adults), 0.92 (considering KB2 for adults), 0.86 (considering KB1 for adults), 0.55 (considering WB1 for adults), and 0.005 (considering WB2 for adults). Similarly, Ba in children accounts for HQ/HI of 0.97 (considering IB1) and 0.87 (considering KB1). HQ/HI shows the highest values for Pb, having 0.99 (considering WB2 for adults) and 0.95 (considering WB2 for children). Non-carcinogenic risk is sure for Ba (considering IB1 and KB2) and Pb (considering WB2). Adults and children living near the mining sites may suffer the adverse effects of heavy metal contamination due to barite mining. HQ/HI for Zn, Cu, and Fe is ≤0.005. The results indicate that some precautionary measures should be taken to avert the potential danger or non-carcinogenic risk of Ba and Pb. In the case of Zn, Cu, and Fe, an adverse health effect is not likely.

Table 6.6: Risk characteristics (hazard quotient (dimensionless) (HQ) and hazard index (HI) (dimensionless)) of heavy metals in mine water and tailing effluents.

Samples	Hazard Quotient (HQ)					Hazard Index
	Ba	Pb	Zn	Cu	Fe	(HI)
(HQ) Adult						
KB1	$\mathbf{1.85 \times 10^{0}}$	$\mathbf{2.56 \times 10^{-1}}$	$\mathbf{1.06 \times 10^{-2}}$	$\mathbf{5.40 \times 10^{-3}}$	$\mathbf{1.32 \times 10^{-2}}$	$\mathbf{2.14 \times 10^{0}}$
IB1	$\mathbf{2.08 \times 10^{0}}$	$\mathbf{5.03 \times 10^{-2}}$	$\mathbf{8.02 \times 10^{-3}}$	$\mathbf{3.52 \times 10^{-3}}$	$\mathbf{6.52 \times 10^{-3}}$	$\mathbf{2.15 \times 10^{0}}$
WB1	$\mathbf{1.50 \times 10^{-1}}$	$\mathbf{5.87 \times 10^{-2}}$	$\mathbf{8.41 \times 10^{-3}}$	$\mathbf{1.47 \times 10^{-3}}$	$\mathbf{5.24 \times 10^{-2}}$	$\mathbf{2.71 \times 10^{-1}}$
KB2	$\mathbf{1.11 \times 10^{-1}}$	$\mathbf{8.41 \times 10^{-3}}$	$\mathbf{1.08 \times 10^{-3}}$	$\mathbf{1.17 \times 10^{-4}}$	$\mathbf{6.96 \times 10^{-4}}$	$\mathbf{1.21 \times 10^{-1}}$
IB2	$\mathbf{1.36 \times 10^{-1}}$	$\mathbf{4.20 \times 10^{-3}}$	$\mathbf{5.87 \times 10^{-3}}$	$\mathbf{5.87 \times 10^{-5}}$	$\mathbf{3.86 \times 10^{-5}}$	$\mathbf{1.46 \times 10^{-1}}$
WB2	$\mathbf{2.94 \times 10^{-1}}$	$\mathbf{5.78 \times 10^{1}}$	$\mathbf{1.46 \times 10^{-2}}$	$\mathbf{8.80 \times 10^{-4}}$	$\mathbf{4.70 \times 10^{-3}}$	$\mathbf{5.81 \times 10^{1}}$
(HQ) Child						
KB1	$\mathbf{1.73 \times 10^{0}}$	$\mathbf{2.39 \times 10^{-1}}$	$\mathbf{9.86 \times 10^{-3}}$	$\mathbf{5.07 \times 10^{-3}}$	$\mathbf{6.06 \times 10^{-3}}$	$\mathbf{1.98 \times 10^{0}}$
IB1	$\mathbf{1.94 \times 10^{0}}$	$\mathbf{4.70 \times 10^{-2}}$	$\mathbf{7.49 \times 10^{-3}}$	$\mathbf{3.29 \times 10^{-3}}$	$\mathbf{2.98 \times 10^{-3}}$	$\mathbf{2.00 \times 10^{0}}$
WB1	$\mathbf{1.40 \times 10^{-1}}$	$\mathbf{5.47 \times 10^{-2}}$	$\mathbf{7.85 \times 10^{-3}}$	$\mathbf{1.37 \times 10^{-3}}$	$\mathbf{2.39 \times 10^{-2}}$	$\mathbf{2.28 \times 10^{-1}}$
KB2	$\mathbf{1.03 \times 10^{-1}}$	$\mathbf{7.80 \times 10^{-3}}$	$\mathbf{1.00 \times 10^{-3}}$	$\mathbf{1.10 \times 10^{-4}}$	$\mathbf{3.18 \times 10^{-4}}$	$\mathbf{1.12 \times 10^{-1}}$
IB2	$\mathbf{1.27 \times 10^{-1}}$	$\mathbf{3.90 \times 10^{-3}}$	$\mathbf{5.48 \times 10^{-4}}$	$\mathbf{5.48 \times 10^{-5}}$	$\mathbf{1.76 \times 10^{-5}}$	$\mathbf{1.32 \times 10^{-1}}$
WB2	$\mathbf{2.74 \times 10^{-1}}$	$\mathbf{5.40 \times 10^{0}}$	$\mathbf{1.36 \times 10^{-2}}$	$\mathbf{8.22 \times 10^{-4}}$	$\mathbf{2.17 \times 10^{-3}}$	$\mathbf{5.69 \times 10^{0}}$

6.4 Discussion

The barite mines are moderately to severely polluted by Ba and Fe and extremely polluted by Pb, whose samples' Igeo showed high values (i.e., WB2, WB1, KB1, and IB1). Similar studies have shown that surface water and soil in a gold mining site may be moderately to heavily polluted by Pb and severely polluted by Cu and Zn (A. J. P. Adewumi & Laniyan, 2020; Hadzi et al., 2019b). High Igeo values might be attributed to artisanal and small-scale mining activities and anthropogenic removal of the heavy metals within the mining sites. Pb and Ba concentration in tailing digestates exceeds the limit of drinking water. Research has shown that Pb concentration in artisan gold mining sites (Pb > 131 mg/L) is higher than the highest values (i.e., 0.6897 mg/L in WB2) reported in this study [11,23,89]. Although Pb concentration reported in this study is minimal, Pb accumulation in humans over a long time may increase blood lead level (BLL) and result in fatigue. High BLL has been reported to cause muscular weakness, damage to body organs, and death of children (Tokalıoğlu et al., 2018). Similarly, a high concentration of barium in water causes vasoconstriction, alters nerve reflexes, results in muscle weakness, and damages the myelin sheath when Ba binds with sulfate and lead (Pb) (Brenniman et al., 1979; WHO, 2004).

The contamination assessment studies on mine water and tailing effluents collected in August 2017 and August 2019 (rainy season) showed that the total toxic unit (TU) for the heavy metals was below the allowable limit (TU < 4). However, the chronic risk level characterization based on the HQ revealed a low chronic risk level (considering short-term risk assessment). HQs and HIs uncovered that Ba and Pb, in some instances, pose a relatively low health risk and can contribute medium to high health risk in other artisanal barite mining sites. The estimated health risks of heavy metals per kilogram of body weight of children are higher than adults.

The presence of Ba and Pb in KB2 and IB2 poses a relatively low risk to health which shows that some precautionary measures should be taken to avert disaster. However, Ba in KB1 and IB1 and Pb in WB1 will contribute medium to high risk (for 1 < HQ < 4, and HQ > 4). Thus, an adverse effect due to the non-carcinogenic risk is expected. It is estimated that residents of the mining sites may consume more heavy metals in water than miners who reside within the neighbouring communities. The maximally exposed individuals (MEIs) are the children, miners, and residents of the mining sites and are more at risk of toxic heavy metals. It is vital that barite mining is carried out responsibly, respecting local and national mining laws and global environmental standards.

6.5 Conclusions

This study identified Cd, Zn, Ba, Cu, Pb, and Fe as major contaminants that cause water pollution due to artisanal baryte mining. The chemical parameter Cd was not detected (concentration lower than the LOD). In this study, it appears that the heavy metals with concentrations above the limits were Fe, Ba, and Pb. Cu and Zn showed low concentrations, always below the permissible values (Zn and Cu) or even close to zero (Cd). Ba, Pb, and Fe tailing effluents and mine water samples will probably contaminate rivers used by miners and surrounding mining communities. ICP-MS results show that the concentrations of Ba and Pb, among other heavy metals, are above the allowable limits stated by WHO, EU, US EPA, CMHNS, NIS, and NSDWQ. The chronic daily intake (CDI) assessment revealed that the accumulation of heavy metals through ingestion and the dermal pathway is possible and can initiate chronic diseases in humans over a long time.

Aside from environmental influences, artisanal mining also contributes additional risks that jeopardize miners' well-being and the entire mining environment. The study recommends that some precautionary measures be taken by miners, environmental and health specialists, owners of mining sites, and mine inspectors to avert disaster and, in some situations, signal an adverse effect due to the non-carcinogenic risk is expected. Therefore, it is concluded that barite mining should be carried out responsibly, respecting local and national mining laws and global environmental standards. Affordable water filters or carbon filters specifically designed to remove lead and Ba will help reduce the quantity of heavy metals consumed in drinking water. Other water treatment methods such as reverse osmosis and distillation can also serve as alternatives recommended by the centre for disease control.

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7.0 CHAPTER SEVEN: CONTRIBUTION TO KNOWLEDGE, CONCLUSION AND FUTURE WORK

7.1 Contribution to Knowledge

The following points have been summarized as the significant contributions of this study to the existing body of knowledge. These are either a piece of new knowledge or modification to the existing body of knowledge:

i. The study showed that on-the-site processed barite has lower heavy metal contents compared to industrially accepted barite and can serve as a potential replacement for barite used by oil drilling mud;

ii. Scientific understanding and explanation of shear stress-shear rate relationships and the viscosity behaviour of the drilling mud due to the addition of baryte as a weighting agent;

iii. The study demonstrated that fine particle complex ores can be beneficiated or concentrated by jigging to increase the specific gravity of the baryte. This is because a higher mineral degree of liberation improves the separation efficiency and quality of jig concentrates;

iv. The study also supports the fact that jigging cannot improve the quality of coarse jig concentrate/increase the assaying of value minerals in the ore despite the high recovery and yield;

v. Higher jig amplitude and lower jig frequency was preferred for small-size baryte ore using fabricated split-columns laboratory mineral jig;

vi. New knowledge on the performance of laboratory-built mineral jig for fine-particle separation ;

vii. The study demonstrated that laboratory-built mineral jig with split-columns could be used to concentrate fine-particle complex ores-containing barite;

viii. The study proved that barite concentrate processed using laboraotry-built mineral jig could replace the industrial-grade barite as a weighting agent in oil drilling applications

ix. The study verified the size and density effects of baryte ores on the separation efficiency, yield, and recovery of baryte and non-baryte minerals;

x. Results of the study, when commercialized, and further recommendations from the current research, will reduce over-dependency on imported/industrial grade barite and imported mineral processing devices;

xi. Development of mining hazard map of Nigeria for defining potential hazard zones and areas prone to high-level exposure to heavy metal contamination and environmental pollution by artisanal barite mining;

xii. The study showed that baryte ponds and tailing effluents is rich in heavy metals, and hence heavy metal contamination due to artisanal barite mining can cause an adverse health implication for miners and, mining community and contribute medium to high health risks via oral ingestion and dermal pathway;

xiii. The study established that artisanal and small-scale miners who do not use safe mining tools during mining are hence prone to health risks, consequences of heavy metal contamination, and environmental pollution;

xiv. The information-sharing framework on safe mining can help strengthen existing but weak mining policies and guarantee safe mining;

xv. The study indicated medium-level non-carcinogenic risks of Ba and Pb, elevated non-carcinogenic risks due to Pb contamination, and a possibility of Pb accumulation over a long period;

xvi. The significance of safe mining and environmental impact assessment on post-mineral extraction processes was demonstrated in this study;

7.2 Conclusions

Relevant conclusions arising from the combined review, design, theoretical, experimental, and analytical study are the following:

a. The detailed analysis and characterization of locally processed barytes in Nigeria are significant. It helps to appreciate the quality of mineral concentrates produced by local mineral processors and gain the acceptance of the drilling industry.

b. The addition of locally processed barytes as a weighting agent in oil drilling mud will help meet the need of the Nigerian oil industry and substitute or serve as a partial replacement for imported or industrially accepted barytes.

c. A new understanding of the structural modification of the baryte-water interface (in the drilling fluid) is of utmost importance and helps control mud weight and optimize the performance of the drilling fluid

d. Fabrication and use of a laboratory-built mineral jig for local baryte processing is timely as it encourages sustainable baryte processing and envisioning responsible mineral extraction in Nigeria in line with sustainable development goals (SDGs) 12

e. A separated, water-jigging columns-laboratory built mineral jig can process a small quantity of fine particles complex ores-containing barytes.

f. Low jig frequency and higher jig amplitude are preferred for higher separation efficiency of small-size (+150-75 µm) baryte particles during jigging.

g. Timely safe mining and environmental impact assessment as part of post-mineral extraction processes will help address ongoing mining hazards and inform mining regulatory agencies on the need to review existing policies and the society on dangers of illegal mining. This ensures the actualization

h. Indigenous fabrication of mineral processing devices in Africa to process Africa ores and solve peculiar African problems is a step in the right direction and worthwhile.

i. The findings of this study demonstrate the potential application of locally processed barytes by fine-particle jigging for a weighting agent in oil drilling application.

j. The adjustment/optimization of jigging conditions does not increase the separation efficiency of coarse feed.

k. Baryte ores with smaller particle sizes gave the highest baryte quality and separation efficiency.

l. Routine heavy metal contamination assessment serves as a regulatory drive towards ensuring the prevention of adverse non-carcinogenic risks and environmental pollution in line with the sustainable development goals (SDGs) 3 for 12 & 13.

7.3 Future work

This study examines fundamental issues and seeks to understand the science that explains the principle of mineral processing by jigging, solid-liquid interface and solid-solid flow. It used a laboratory-size laboratory-built mineral jig, and the jigging conditions were randomly selected. Results obtained from the study showed some potentials of Nigerian barytes as a weighting agent in drilling mud. Similarly, the laboratory-built mineral jig gave a maximum separation efficiency of 16%. The study is a work in progress and has demonstrated certain possibilities that require further investigation. There is a need to fabricate a prototype mineral jig from the existing laboratory-built design that allows adequate or wide-range selection of jigging conditions and optimization of the jigging process. The quantity of quartz and hematite in the jig concentrate is higher than the value recommended by the American Petroleum Institute (API).

Similarly, the jig tailings/overflow contains ~ 6% to 10% of the total baryte in the ore and water-soluble salts. Further study is required to recover value minerals from the tailings and reduce quartz and hematite from the jig concentrates. The effect of adding laboratory-processed barytes as a weighting agent in drilling mud was not considered in the current study. Also, the influence of water flow rate, water upward velocity, mineral bed thickness, jigging time, a wide-range variation of jig amplitude and frequency should be demonstrated in further studies. Future work will optimize process conditions of the laboratory-built mineral jig, develop prototype mineral jigs, and small-scale baryte processing for drilling mud and other industrial applications. Additional works will address the welfare of miners through medical outreaches, seminars, and tests, training on mine development and safety. This is entirely an outreach program. The exhibition of different baryte grades, prototype mineral jig design, and a small-scale baryte processing plant is necessary to demonstrate the quality of locally processed baryte and its comparison with the industrial-grade/imported baryte.

Appendix A

Table A1: Risk contribution of heavy metals in mine water samples and tailing effluents.

Elements	Kp or Pc (cmh^{-1})	RfD_{ing} $(mgkg^{-}$	RfD_{derm} $(mgl$	References
Pb	0.0004	0.0014	0.00042	[46]
Ba	0.003	0.07	0.000062	[46,49]
Fe	0.001	0.7	0.14	[46]
Cd	0.001	0.0005	0.000025	[23,46]
Cu	0.001	0.04	0.008	[46]
Zn	0.0006	0.03	0.06	[46,72]

Kp or Pc is the partition/permeability coefficient; RD is the same as RfD: reference dose.

Table A2. Risk contribution of heavy metals in mine water samples and tailing effluents.

Elements	Inhalation RfD	Oral CSF	Dermal CSF	Inhalation CSF	References
Pb	NA	0.0085	NA	420	[47,49,72]
Ba	0.0076	ID	ID	ID	[23,46]
Fe	NA	NA	NA	NA	[46,47]
Cd	0.000057	NA	NA	6.3	[23,49]
Cu	NA	NA	NA	NA	[23,49]
Zn	NA	NA	NA	NA	[49,72]

[23,46,47,49,72]=(Agency, 2006; U. S. EPA, 2004; Gholami et al., 2020; NIS-554-2015, 2015; Standardization, 2007)

ID: inadequate data, NA: not available, CDF: carcinogenic slope factors.

Table A3. Exposure factors for the health risk assessment of heavy metals in mine water samples and tailing effluents.

Parameters	Unit	Child	Adult/Resident	Worker	References
Body weight (BW)	kg	15	70	70	[23,49]
Contact rate (CR)	L/day	1.0	2.0	1.0	[77]
Exposure factor (EF)	days/year	350	350	250	[49]
Exposure duration (ED)	years	6	30	25	[43,49]
Exposure time (ET)	days	2190	10950		[44,49]
Exposure frequency (ER)	Days/year	365	365	365	[23,49]

Ingestion rate (IR or I_R)	mg/day	200	100	[49]
Inhalation rate (IRih)	$\mathbf{m^3/day}$	10	20	[49]
Skin surface area (SA/EA)	cm^2	2100	5800	[49]
Soil adherence factor (AF)	$\mathbf{mg/cm^2}$	0.2	0.07	[43,49]
Dermal adsorption factor (ABS)	none	0.1	0.1	[23,49]
Dermal exposure (FE)	none	0.61	0.61	[49]
Particulate emission factor	$\mathbf{m^3/mg}$	1.3×10^9	1.3×10^9	[49]
(PEF)				
Conversion factor (CF)	$\mathbf{kg/mg}$	$\mathbf{10^{-6}}$	$\mathbf{10^{-6}}$	[23,49]
Average time (AT)				
For carcinogens	days	365 × 70	365 × 70	[49,77]
For non-carcinogens		365 × ED	365 × ED	[49,77]

Table A4. Mean metal concentration in analyzed samples and the maximum tolerable daily intake in drinking water (A. J. P. Adewumi & Laniyan, 2020; Agency, 2006; Brenniman et al., 1979; Daburum et al., 2019; U. S. EPA, 2004; Melekestseva et al., 2014).

Samples/Standards	Zn (mg/L)	Cu (mg/L)	Fe (mg/L)	Ba (mg/L)	Pb (mg/L)
KB1	0.027	0.0185	0.7895	11.055	0.0305
IB1	0.0205	0.012	0.389	12.4035	0.006
WB1	0.0215	0.005	3.1245	0.8915	0.007
KB2	0.00275	0.0004	0.0415	0.659	0.001
IB2	0.0015	0.0002	0.0023	0.8132	0.0005
WB2	0.0373	0.003	0.2829	1.7500	0.6897
WHO	3.000	2.000	0.300	4.000	0.010
EU	3.000	2.000	0.300	0.700	0.010
NIS	3.000	2.000	0.300	0.700	0.010
US EPA	5.000	1.300–3.000	0.300	2.000–4.000	0.005
CMHNS	NA	NA	0.050	NA	0.010–1.000

NA: not available

Table A5. List of the LODs of the inspection method, relevant information about the validation, and analysis condition parameters.

Elements Examined	Limit of Detection (LOD) (ppm)	Limit of Quantification (LOQ) (ppm)
Ba	0.000693	0.29907
Cu	0.000693	0.30207
Fe	0.0001287	0.29312
Pb	0.000429	0.29804
Zn	0.000858	0.29508

$$\mathrm{LOD} = \frac{3.3\, RSD}{S}$$

$$\mathrm{LOQ} = \mathrm{LOD} + R$$

where LOD is the limit of detection, LOQ is the limit of quantification, RSD is the standard deviation (obtained from ICP-MS), and R is the validated lowest spike recovery (obtained from ICP-MS). The equations are used in line with standards and published articles (Fry et al., 2020; Tepanosyan et al., 2020). Condition parameter: collision–reaction interface (CRI), $R^2 > 99.6\%$ accuracy as shown on the calibration curve.