FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 4 No. 2, June, 2020, pp 645 – 657
DOI: https://doi.org/10.33003/fjs-2020-0402-199

DIRECT BIOLEACHING OF ZINC USING manihot esculenta crantz (cassava) EXTRACT WITHOUT ADDITIVES

***[1,3]Ajibola, O. O., [1]Adebayo, A. O., [1]Borisade, S. G., [1]Adegbenro, A. E., [2]Oloruntoba, D. T. and [3]Olubambi, P. A.**

[1]Department of Materials and Metallurgical Engineering, Federal University Oye Ekiti, Nigeria
[2]Department of Metallurgical and Materials Engineering, Federal University of Technology, Akure, Nigeria
[3]Centre of NanoEngineering and Tribocorrosion, University of Johannesburg, Johannesburg, South Africa

*Corresponding Author's Email: olawale.ajibola@fuoye.edu.ng +2348068790679

ABSTRACT

The advent and development of new technologies that will provide better yields, cleaner and a safer environment is a global challenge for the researchers. Traditional solvents used in extraction of minerals are at many times hazardous thereby constituting threats to the ecology. The work reports the direct bioleaching of zinc sourced from Abakaliki-Ishiagwu complex zinc sulphide ore deposit. The sphalerite ore is predominant in Zn with other associated metals Pb, Cu, Fe, Ni, Sb, As, Cd, Au, V, Co, Ag, K, Al and Ca. It covers the pre extraction processes of mineral comminution (crushing and grinding); separation by froth flotation; and roasting. Agro-cyanide was extracted from cassava plant (Manihot esculenta Crantz) leaves and was used as leachant without any additive. The result of atomic absorption spectrometry (AAS) analysis of the leached liquor (pregnant solution) shows that lead, copper and iron in addition to Zinc, were obtained from the leached ore roast at 149.25 ppm (Zn), 79.25 ppm (Pb), 0.25 ppm (Cu) and 4.25 ppm (Fe) extraction after 21 days. Elongated contact of ZnO ore is not encouraging for Zn extraction as there is a decline in the quantity of Zn, Fe and Cu as the leaching time (days) increases. The mechanism of the Leach next faction is yet to be fully ascertained, hence the need for further work in the area.

Keywords: direct bioleaching, zinc ore, Manihot esculenta Crantz, leach extraction

INTRODUCTION

Zinc ore is usually mined below the earth surface as sphalerite in which zinc is found alongside with lead as galena. Some other zinc containing minerals include hemimorphite, hydrozincite, calamine, frankline, smithsonite, willemie and zincite. In Nigeria, large complex ore deposits of zinc and lead are found at Abakaliki (Victor et al. (2015; Obarezi and Nwosu, (2013); Okafor and Uwadiale, (1997); Akande and Mucke, (1989)). The level of exploration and exploitation of the mineral deposit is far below the reality. The ore is only mined for export leaving the local industries which may need the final products to suffer. The after effect is that zinc products such as galvanized steel sheets are very expensive for common man. Like every other ore, beneficiation is an essential route for obtaining clean minerals from the locked up ore constituents. This often involves comminution and concentration of the desired mineral values from the unwanted gangues. Several attempts have been reported on the beneficiation of some of the numerous available ores on the laboratory and experimental scale (Egunlae et al. (2006); Ajibola et al. (2015)). The amenability of the ore to extraction is also an important factor of consideration. This may be singularly carried out or in combination of the pyrometallurgy, hydro-metallurgy and/or electro-metallurgical route. For effective results, sulphide ores are converted wholly or partially by roasting to oxides or sulphates. The desired metal values must be easily reduced by fire or digest in and recoverable from the solution. Different forms of roasting mechanism may be applicable in this typical complex sulphide under study; there may be oxidizing roast or burning out of sulphur from sulphide ores which are then replaced wholly or in part by the oxide.

$$2MS + 3O_2 \rightarrow 2MO + 2SO_2 \quad [1]$$

Volatising roast- the elimination of other elements with volatile oxides such as As_2O_3, Sb_2O_3 or even ZnO which can be recovered as fume; conversion of certain metallic sulphide ores to sulphate; reduction roast at elevated temperature may produce metals from the interaction of oxides and sulphides.

$$MS + 2MO \rightarrow 3M + SO_2 \quad [2]$$

There have been diverse reports of the beneficiation and extraction of zinc by conventional methods using active acids, bases and cyanides in the literatures (Onyemaobi (1990); Oluwaseyi and Egunlae (2007); Egunlae et al. (2006); Egunlae and Oluwaseyi (2007); Jimoh and Egunlae (2010); Ajibola and Jimoh (2014); Ajibola et al. (2015)). Both pyro-metallurgical and hydro-metallurgical methods have been used for extraction of zinc from rich ore or residues (tailings) (Chen et al. (2009)). Recently, there are some reports that zinc oxide ores can be treated by flotation (Onal et al. (2005); Ejtemaei and Irannajad (2008); Irannajad et al. (2009); Ejtemaei et al. (2011)) and by bio-hydro-metallurgical methods (Meshkini et al. (2011)). Although the results obtained by these methods showed that the efficiency is comparable with usual methods, the technology certainly needs further follow-up.

Many studies on leaching of zinc oxide ores by acid and basic solution have been published. In recent years, the leaching of zinc ores containing oxidized minerals such as carbonates or silicates with sulphuric acid and its kinetics has been investigated. He et al. (2010), Cun-xiong et al. (2010) and Xu et al. (2010) focused on pressure leaching. The amount of zinc extraction in sulphuric acid solution is high in comparison with other methods and the concentration of silica and other unwanted elements are low. Espiari et al. (2006) studied the zinc dissolution kinetics of smithsonite and hemimorphite in the lead flotation tailings by sulphuric acid. Zhao and Stanforth, (2000) produced zinc powder by use of the alkaline leaching process on smithsonite. The work extracted over 85% of both Zn and Pb, and less than 10% of aluminium using 5 M NaOH solution as the leaching agent in which zinc, lead and aluminium come into solution as $Zn(OH)_4^{-2}$, $Pb(OH)_4^{-2}$ and $Al(OH)_4^{-1}$ respectively. Similar to this study, Chen et al. (2009) investigated the parameters affecting the process of leaching refractory hemimorphite $[Zn_4(Si_2O_7)(OH){\cdot}H_2O]$ zinc oxide ores with NaOH solution. The maximum zinc extraction in optimum conditions was reported to be 73% of zinc content of the ore.

Traditionally, zinc is produced from sphalerite (ZnS) using roasting, leaching and electrolysis (RLE) methods, releasing unwanted SO_2 gas to the environment. Direct Atmospheric Leaching (DAL) and pressure leaching (PL) are two newer methods with a similar approach, except that pressure leaching is carried out under high pressure

Egunlae et al. (2006) worked on selective flotation of galena from the Isiagwu-Abakaliki area lead-zinc sulphide complex ore using some locally sourced plant oil extracts: pine oil (PNO), groundnut oil (GNO), palm kernel oil (PKO), and castor oil (CAO). From the result, these refined local plant oil was profitably used in floating galena from the Isiagwu deposit with better yields when the GNO, PKO were de-colourised ('refined') at elevated temperatures by passing the oils through a column of heated animal charcoal made from burnt bones. The suitability of some of such oils has been reported for froth flotation of different minerals (Nwoke (1997)).

Ajibola and Jimoh, (2014) reported the laboratory studies on lead and zinc recovery from the Abakaliki complex sulphide ore by roasting in air prior to leaching in three mineral acids HF, HCl and H_2SO_4 with agitation varying the leaching time and molar concentration of acids. In all instances, increasing concentration reduced the dissolution of Pb in H_2SO_4 as the acid concentration increased was affected by the presence of large impurities of higher or lower electropositivity than Pb and Zn in the electrochemical series. Ajibola et al. (2015) had investigated leach-electrowinning behaviour based on the mineralogical and geometallurgical properties of the complex lead-zinc sulphide porphyritic ore deposit; to determine the suitability of leach-electrowinning method for the extraction of zinc in boosting the local production of zinc metals in Nigeria. Among others, Egunlae and Jimoh, (2010) reported the leaching of gold ore in cyanide. Nonetheless, literature is very scarce on the use of bioleaching of zinc derived from the cassava sourced agro-cyanide. Fortunately, cassava as reliable source of agro-cyanide is produced annually in a very large quantity in Nigeria. Hence, there is a need to exploit the opportunity in the extraction of zinc. The extraction of zinc from its ore using the cassava fluid extract entails some common basic steps of comminution and separation methods.

The species of cassava cultivated for food in Nigeria is *Manihot esculenta*. There are several thousand varieties of cassava and about 100 related wild species (Hershey et al. (1997)) with hydrogen cyanide (HCN) contents of their roots ranging from 1-1550 parts per million (ppm) (Cardoso et al. (2005). Cassava plants are generally categorized as bitter or sweet, depending upon their cyanide content. It contains two naturally occurring, but potential toxic compounds. These are the cyanogenic glycosides which releases hydrogen cyanide (HCN) as a result of enzymatic hydrolysis following maceration of the plant tissue, - linamarin and lotaustralin, the former being present in much larger quantities, usually up to 90% of the total content. The low-HCN, or sweet cassava, has less than 50 ppm of cyanogenic equivalents, while the high-HCN or bitter cassava has more than 100 ppm (Wilson and Dufour (2002). According to Adepoju and Nwangwu (2010), the food value of cassava is greatly compromised by its toxic hydrogen cyanide content. The sweet cassava can be cooked and eaten as they are, while the bitter cassava needs to be processed before being consumed.

The present research is carried out with the view to leaching zinc ore using agro based cyanide from cassava fluid extract and determine the amount of metal dissolution in the bio-fluid extract. Reports are available on the extraction of gold and silver using cyanide or agro cyanide base fluid (Burstall et al. (1953); Razanamahandry et al. (2017). On the other hand, information is very scarce on the use of agro cyanide or bioleachant in the extraction of zinc. Information is also available on the zinc extraction using NaOH, H_2SO_4 and HCl (Oluwaseyi and Egunlae (2007); Ajibola and Jimoh (2014); Ajibola *et al.* (2015), whereas, little or no work has been conducted using natural organic agro cyanide base leachant sourced from cassava fluids. Hence the current study is undertaken on bioleaching of zinc using cassava leave extracted juice. Bioleaching is referred to as mobilization of the ions from ores using biological oxidation reactions. Generally, this method is used to extract valuable metals such as copper, nickel and gold from complex, resistant, low grade and less pure ores. In these decades, there has been increased attention to bioleaching, because of its less cost and being environmentally friendly.

METHODOLOGY

Characterization of ore

As-mined complex lead-zinc sulphide ore sample was procured from Minerallex Ltd., Abakaliki in Ebonyi State, Nigeria. The mineral phase analysis was performed with the aid of x-ray diffraction (XRD) technique, (RIGAKU Ultima IV model). The microstructures and particle size properties were examined via scanning electron microscope (Vegas 3 Tescan SEM model) with energy dispersive X-ray spectrometer (EDS) attachments and INCA X-Stream 2 pulse analyzer software installed. The elemental composition of the as-mined ore, froth and roast were chemically characterized using x-ray fluorescence (XRF) in conjunction with the EDS. Whereas, the composition and quantity of the extracts in solution were determined by atomic absorption spectrometry (AAS). Electronic weighing balance (Schimadzu AY120 model measuring to 0.0001 g) was used to measure mass of extracts

Comminution: Crushing and grinding of ore

The equipment used includes the Denver laboratory size jaw crusher and ball mill; sieve shaker. A total of 5000 g of the as-mined sulphide ore was crushed and ground by using the jaw crusher, pulverizer and ball mill respectively (Figure 1a-c). The ore was sieved and separated to particle sizes between -125+75µm and -800+150 µm using a set of eight sieve apertures (850 µm, 600 µm, 425 µm, 300 µm, 150 µm,125 µm,106 µm, 75 µm and pan). Thereafter, 1000g of -125+75 µm particle size (regarded as fine size) was taken for each batch of froth flotation process.

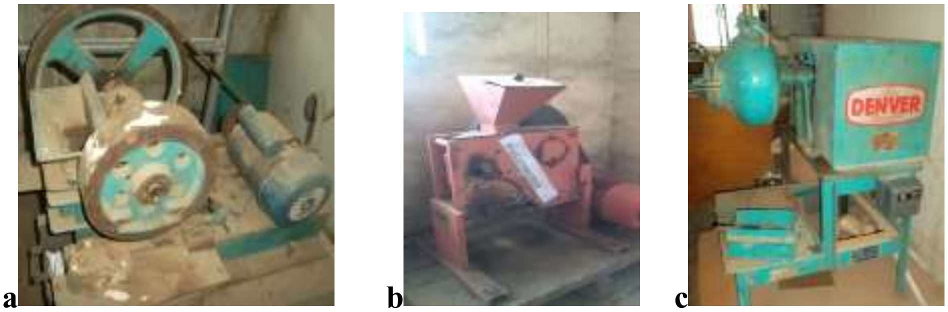


Figure 1: (a) Jaw Crusher, (b) Pulverizer and (c) ball mill (*Ajibola et al., 2015*)

Froth floatation and direct atmospheric roasting processes

1000g ore was weighed and floated per batch of the froth flotation while the flotation process was carried out using Denver D.12 sub-aeration flotation machine at 40% pulp density. The methyl-isobutyl-carbinol [$(CH_3)_2CHCH_2CH(OH)CH_3$] is commonly used as frother (for both non-ferrous metal (Pb-Zn, Cu-Mo and Cu-Au) and some non-metallic ore constituents) due to its excellent foaming characteristics. Sodium oleate ($C_{18}H_{33}NaO_2$) was used as the collector and calcium oxide (CaO) as the pH regulator. Sphalerite (ZnS) was recovered as concentrate while other minerals and impurities were depressed as tailings. Drying of ZnS froth concentrate was performed using Vacutec Labconco Rapidvap dryer.

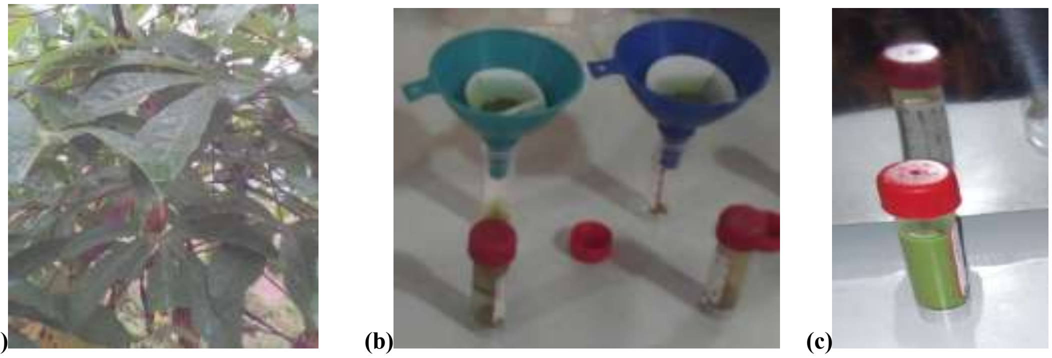
About 500g of the dried sample of the concentrate obtained from the flotation was roasted to a constant weight in an electrical resistance furnace at 750~800 °C for 3 hrs under excess atmospheric air condition (Figure 3). The ore was removed from the furnaces, cooled to room temperature and reweighed. The weight loss method was used to assess the volatile matter content of the ore (Table 3)

Figure 2: (a) flotation of sulphide ore using (b) Denver sub-aeration flotation machine

Figure 3: Roasting of ore in electric furnace (Nabertherm® 1300 ºC)

Extraction of cassava fluid and preparation

The *Manihot esculenta Crantz* (Cassava) leaves (Figure 4a) were obtained at farms located within the Federal University Oye Ekiti, Ikole campus in Ikole Ekiti, Nigeria. The cassava leaves were plucked freshly from the stands and kept in plastic bags. The leaves were rinsed thoroughly with distilled water and pounded with the mortar and pestle to soften them. The mast of pounded leaves was squeezed to extract the leaf juice and the juice was drained into a clean plastic bowl. The extracted leaf juice was filtered through the screen (filter paper) aperture -20 µm (Figure 4b). The filtrate was subjected to vigorous centrifugal stirring and to allow fast settling of micro fine particles in the extract juice for about 4 hours, after which it was decanted to get clean and clear fluid. The leaf extract or filtered juice (Figure 4c) was divided into four different plastic cylinders to the 60 ml gauge.



(a) **(b)** **(c)**

Figure 4: (a) Cassava leaves, (b) Filtration of fluid extract and (c) extracted juice

Leaching of zinc ore in cassava fluid

20 g of roasted ore was weighed into each of the 100 ml plastic cylinders containing 60 ml of the filtered cassava leaf juice extract without the addition of other reagents such as inhibitors, deoxidizer, pH regulator and buffer, etc. The bio-extraction was performed at 20 g/60 ml fluid extract for various leaching time intervals of 7, 14 and 21 days. After the expiration of each leaching period, the pregnant solution was obtained by filtration and taken for chemical analyses using Atomic Absorption Spectrometer (AAS) to determine the amount of Zn, Pb, Ni, Cu and Fe that dissolves at due date. The flowchart for direct zinc bioleaching extraction process is illustrated in Figure 5.

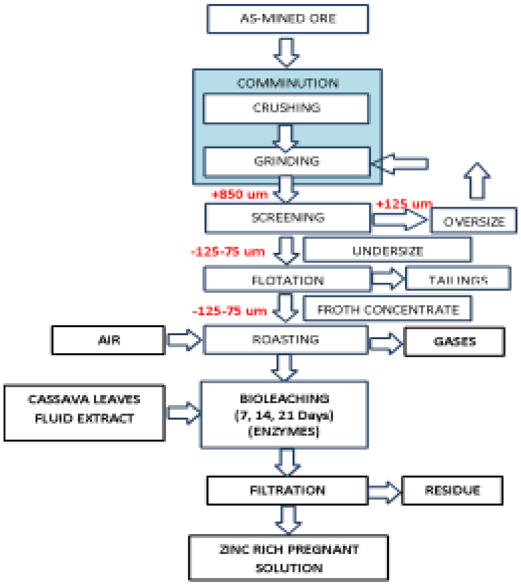


Figure 5: Flow chart for direct Zinc bioleaching extraction process

RESULTS AND DISCUSSIONS

In discussing the various results obtained from the bioleaching experiments, some assumptions and speculations are made based on their correlation with the three major chemical analyses (XRF, AAS, EDS and XRD) used in the work.

Composition of concentrate sample

The XRD analysis also shows morphology of mineral constituents in the complex ore. The XRF and AAS (Table 1) show that more than 19 metals were present in the ore concentrate with their various compositions as identified by the XRF (Figures 6a, 6b) and AAS (Figure 6c), while about fifteen (15) different mineral phases were identified in the XRD of the bulk ore (Figure 7). It indicates that the sulphide ore is rich in zinc (Zn) with little amount of lead (Pb). Nickel occurs in the raw ore as silicide and nickel zinc phases. Zinc was found as sphalerite (ZnS) in as mined ore and in addition, sphalerite-ferroan ($Zn_{0.825}Fe_{0.175}S$) in the froth. Copper manifested as sulphide and chalcopyrite while iron mineralized as Rudashevskyite and Pyrite in the as-mined ore. More of the copper minerals are obtained in the concentrate in different phases as Spionkopite ($Cu_{39}S_{28}$), Mooihoekite ($Cu_9Fe_9S_{16}$) and Bornite, (Cu_2FeS_2). The significance and amenability of the sulphide ore to roasting is seen from the XRD results. Zinc minerals transformed to oxide (ZnO); lead is converted to PbO_2. Iron minerals were partly converted to magnetite while Rudashevskyite (FeS) and Chalcopyrite ($CuFeS_2$) were retained. The SEM images (Figures 8) revealed the ore particle morphologies while the EDS diffractograghs (Figure 9) validated the XRF, AAS and XRD elemental components of zinc sulphide ore and the dead roast (ZnO).

Table1: Chemical composition of as-mined sulphide ore by XRF (%) and AAS (ppm)

Bulk	XRF(%)	AAS(ppm)	Bulk	XRF(%)	AAS(ppm)
Ni	ND	30.3	S	20.6929	ND
Sb	ND	50.31	Cl	0.0193	ND
As	ND	42.1	Al	0.2711	791.5
Au	ND	60.4	K	0.0052	351.3
V	ND	3.89	Ca	0.0878	59.4
Ag	ND	17.65	Fe	3.6366	152.56
Ga	0.018	ND	Co	0.0654	3.16
Mg	0.057	ND	Cu	0.0424	69.4
Mn	0.296	ND	Zn	73.1308	785.91
Si	1.3643	ND	Cd	0.201	58.73
P	0.0065	ND	Pb	0.1057	345.62

*ND-Not determined

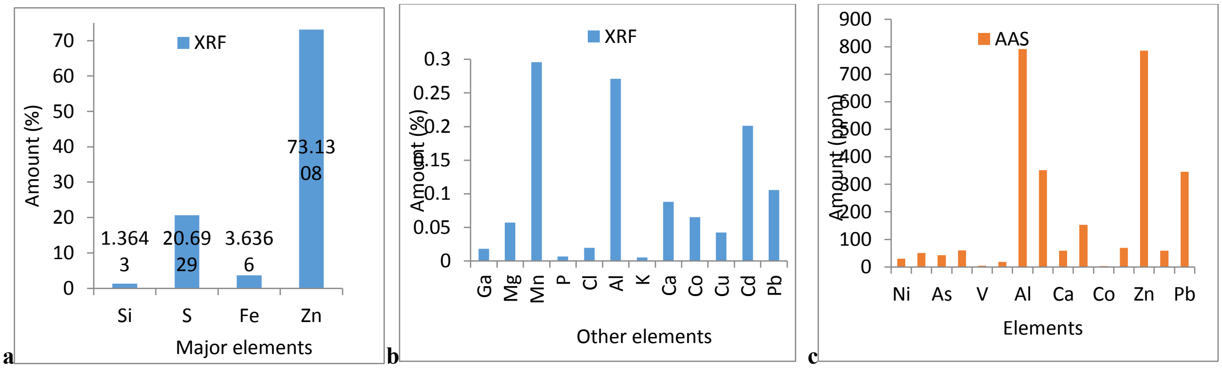
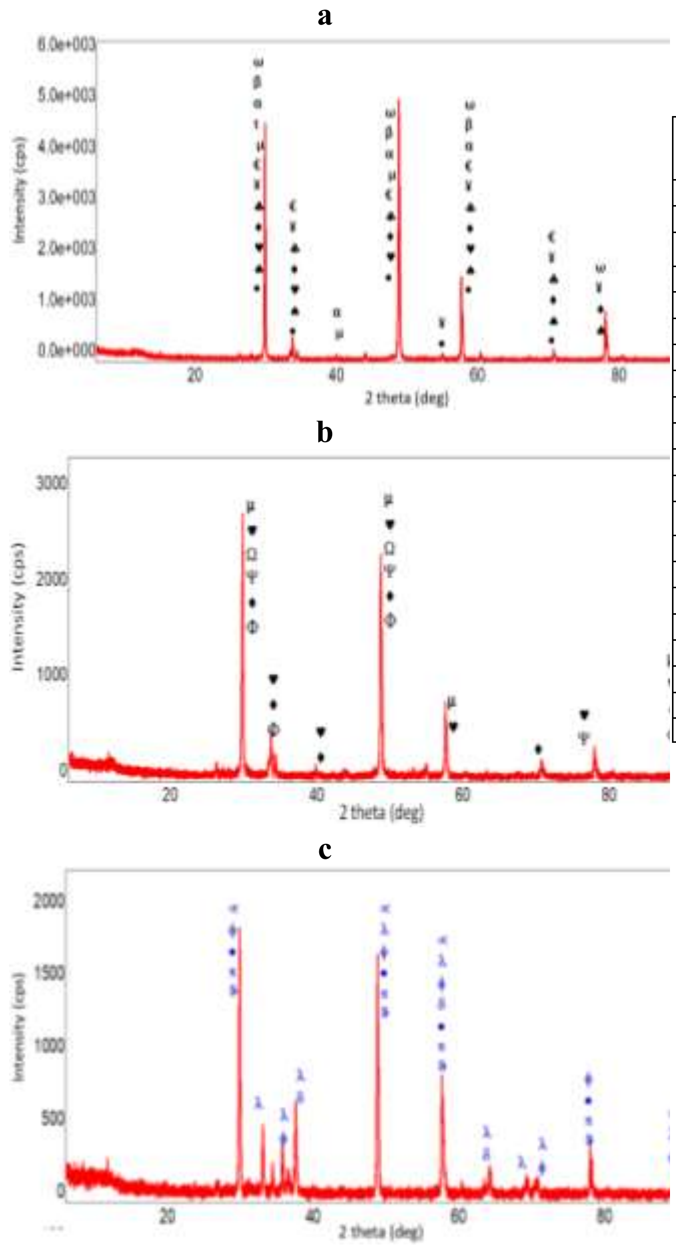


Figure 6: Composition of as mined ore by (a,b) XRF and (c) AAS



Key

Phase name	Formula	Symbol
Nickelsilicide	$NiSi_2$	ω
Silicon,syn	Si	β
NickelZinc	$NiZn_3$	α
CalciumSilicate	Ca_2SiO_4	τ
ZincSulfide	ZnS	µ
CopperSulfide	Cu_2S	€
alpha-SiO2,quartzHP	SiO_2	¥
Rudashevskyite,syn	FeS	♣
Pyrite	FeS_2	♥
Chalcopyrite,syn	$CuFeS_2$	♠
Sphalerite	ZnS	●
Spionkopite	$Cu_{39}S_{28}$	Ω
Mooihoekite,	$Cu_9Fe_9S_{16}$	Ψ
Bornite,	Cu_2FeS_2	♦
Sphalerite, ferroan syn	$Zn_{0.825}Fe_{0}$	Φ
CobaltSilicon	$CoSi_2$	∝
Zincite	ZnO	λ
LeadOxide	PbO_2	ф
Magnetite,	Fe_3O_4	δ
Rudashevskyite	(Fe,Zn)S	π
Chalcopyrite	$CuFeS_2$	ϑ

Figure 7: XRD of mineral phases present in the (a) as-mined, (b) froth and (c) roast

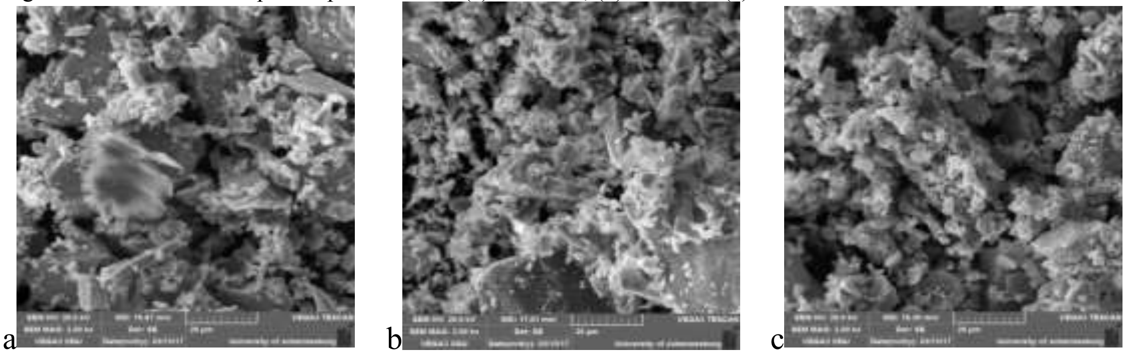

a b c

Figure 8: SEM micrographs showing the morphologies of (a) ZnS rich as-mined ore, (b) ZnS froth concentrate and (c) ZnO roast particles.

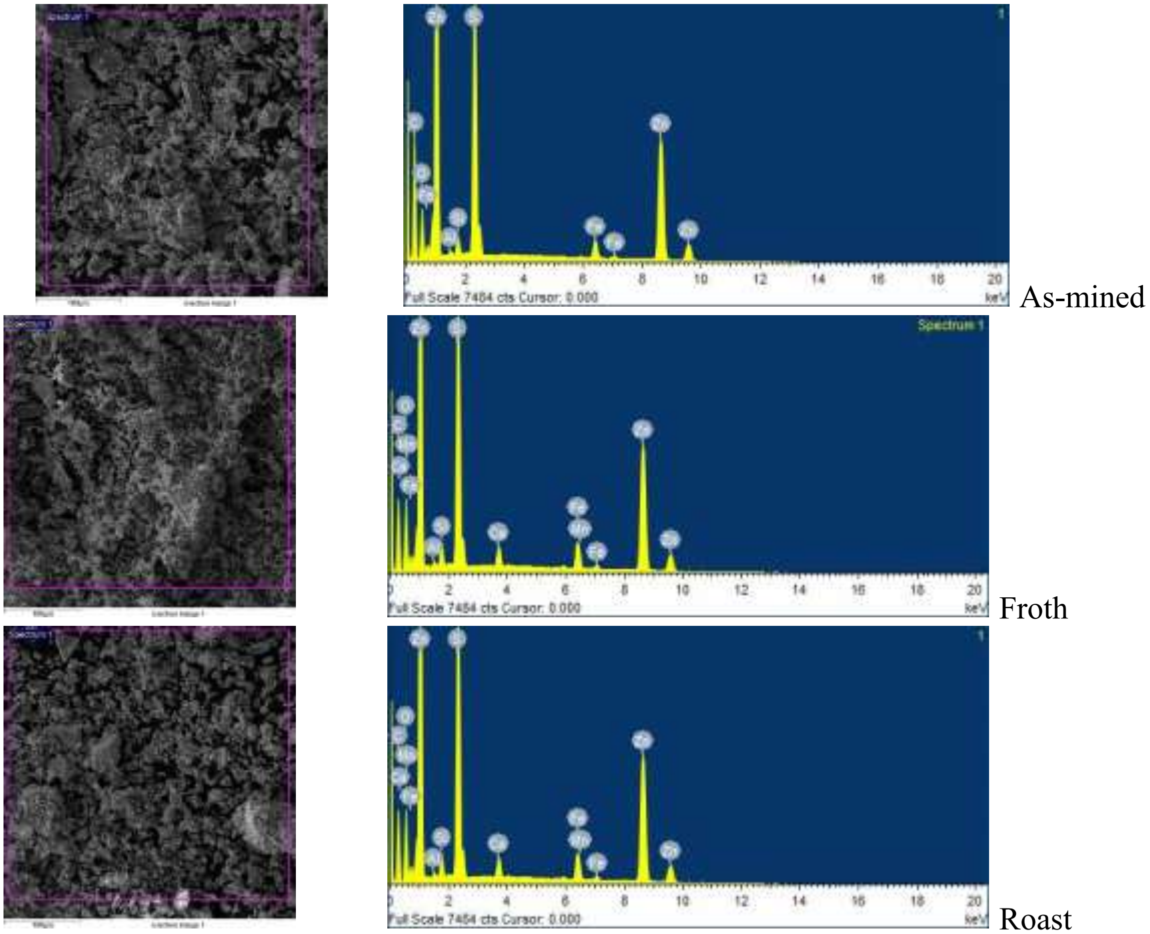


Figure 9: EDS of (a) as-mined, (b) froth and (c) roast of sulphide ore

Comminution characteristics

The size reduction result (Figure 10) by crushing and grinding using pulverizer and ball mill respectively also indicates the coarse particle (+850 to +300 µm range); medium size particle (-300 to +125 µm range) and fine size particle (-125 to -75 µm range) after grindings. It shows that the mineral is soft, producing a large amount of fine particle size. Also the line indicates that the mineral is reducing in size with respect to the time of grinding.

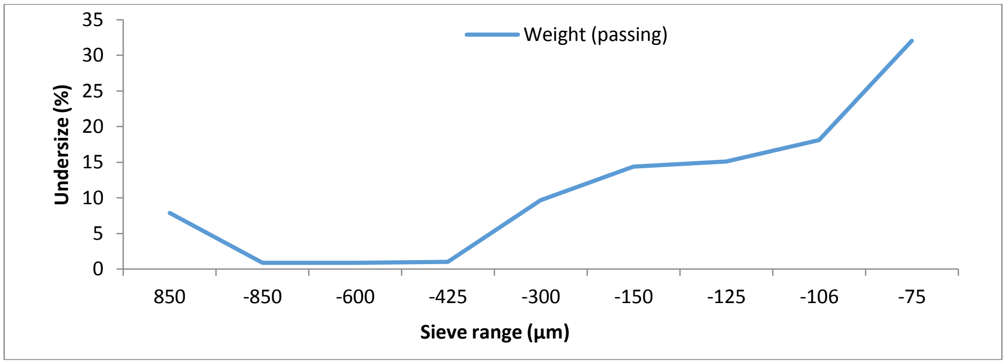


Figure 10: Particle Size analysis of Zinc sulphide ore

Froth floatation behaviour

Three different runs of flotation were performed in batches on the ore using 1000 g of finely ball milled sample taken from the -300 ~ -75 µm particle size range (Table 2). The Figure 11 shows the amount of concentrate received, the tailing as well as the percentage loss in the process. The froth of the concentrate was obtained at 35.7% because much loss (5.1%) occurred as a result of high adhesion between some froth and the surface of the container. The high amount of ore that resulted to the tailings may be due to high amount of gangues and presence of middling containing Zinc that were not fully liberated within the particle size range used for the experiment. The SEM micrographs (Figure 8) compare the morphologies of ZnS rich as-mined ore and ZnS in the froth concentrate.

Table 2: Froth floatation at 40% pulp density

	Feeds (g)	Concentrate		Tailings		Loss	
		Wt. (g)	Wt. (%)	Wt. (g)	Wt. (%)	Wt. (g)	Wt. (%)
Run 1	1000	374	37.4	577	57.7	47	4.7
Run 2	1000	339	33.9	699	60.9	52	5.2
Run 3	1000	358	35.8	588	58.8	54	5.4
Average	1000	357	35.7	592	59.2	51	5.1

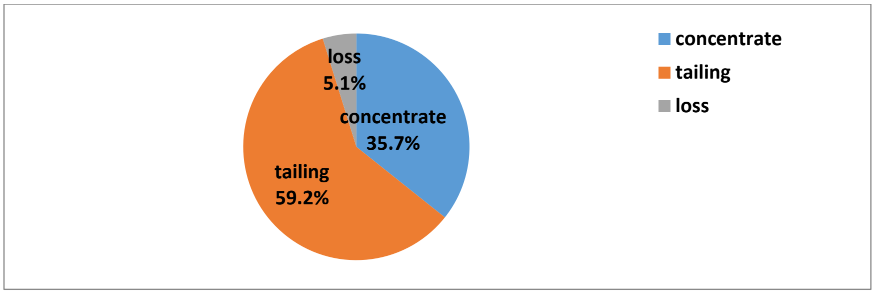


Figure 11: Amount of concentrate, tailing and the percentage loss

Roasting of zinc ore

Table 3: Roasting of the fine ore concentrate.

Feeds	Particle size	Initial wt. (g)	Final wt. (g)	Wt. loss (g)	%Volatile matter
Run 1	(-125+75µm)	500	463.41	36.59	7.32
Run 2	(-125+75µm)	500	450.67	49.33	9.87
Average	(-125+75µm)	500	457.04	42.96	8.59

The amenability of the ore to roasting is presented by the fine particle size used in the work. The roasting released about 8.59% volatile matters (Table 3). Roasting method converted the zinc sulphide ore to oxide and SO_2; and eliminated some of minor elements with volatile oxides such as As_2O_2, Sb_2O_3, etc (3-5):

$$2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)} \quad [3]$$

The XRD validates the conversion of certain Zn, Pb and Fe minerals to oxides in the form of zincite, lead oxide and magnetite, (ZnO, PbO_2, Fe_3O_4) and partially retained as sulphide, whereas Co and Si formed $CoSi_2$.

$$ZnS_{(s)} + 2O_{2(g)} \rightarrow 2ZnSO_{4(s)} \quad [4]$$

$$Co + Si \rightarrow CoSi_2 \quad [5]$$

ZnO and PbO like some oxides will react with common alkaline solutions (such as NaOH) to form zincide and plumbate (Ajibola et al. (2014), (2015). In the previous studies, heat was applied to accelerate the dissolution of lead in NaOH (Ajibola et al. (2014), (2015). This may not be favourable with ZnO digestion in agro-cyanide, since heating effect may destroy the needed microorganisms required in the bioleaching process.

The co-oxidation reactions of copper and iron sulphide to sulphate and oxides are as shown in equations (6-8).

$$CuFeS_2 + 4O_2 \rightarrow CuSO_4 + FeSO_4. \quad [6]$$

$$2CuS + {}^{7}/_{2}O_2 \rightarrow CuO.CuSO_4 + SO_2 \quad [7]$$

$$2CuFeS_2 + {}^{13}/_{2}O_2 \rightarrow 2CuO + Fe_2O_3 + 4SO_2 \quad [8]$$

The possible phases that may be present include Cu_2S, CuS, $CuSO_4$, SO_2, CuO, Cu_2O, Cu, $CuO.CuSO_4$, Fe_2O_3 and $FeSO_4$ at T = 750~800 °C (1023~1073 K).

Part of the lead sulphide might have oxidized to sulphate and oxide during sulphide roasting in the furnace under supply of air [9-13].

$$PbS + 2O_2 \rightarrow PbO_2 + SO_2 \quad [9]$$

$$PbS + {}^{3}/_{2}O_2 \rightarrow PbO + SO_2 \quad [10]$$

$$PbS + 2PbO_2 + O_2 \rightarrow PbSO_4 + 2PbO \quad [11]$$

$$PbS + PbO + 2O_2 \rightarrow PbSO_4 + PbO \quad [12]$$

$$PbS + PbSO_4 + 2O_2 \rightarrow 2PbO_2 + 2SO_2 \quad [13]$$

There is possibility of forming different phases that may include; PbO_2, PbO, SO_2, and $PbSO_4$ at T = 750~800 °C (1023~1073 K).

Extraction of metals from the ore using cassava fluid extract

The atomic absorption spectrometry (AAS) result in Figure 13a shows that the zinc obtained is decreasing with respect to the days of the leaching process, likewise cumulative % loss. This result shows that at 7 days, 14 days and 21 days; 150.25, 149.50 and 149.25 (in ppm) of zinc was dissolved respectively in the cassava leaves extract that was used to digest the roasted ore.

The cumulative % loss shows the progressive rate at which the lead was decreasing with respect to the leaching time (days). Hence, it is advisable to reduce the days of leaching because the cyanide is more active at the early days of leaching and before the growth of Pseudomonas Sp., which reduces the cyanide content in the cassava leaf extract (Akcil et al. (2003)) and it also consumes the zinc produced. However, Figure 13b revealed in the case of lead that it was increasing with respect to the days of the leaching process, likewise its cumulative % loss. This result shows that 55.25, 62.25 and 79.25 (in ppm) of lead was dissolved at 7 days, 14 days and 21 days respectively in the cassava leaves extract. The cumulative % gain shows the progressive rate at which the lead is increasing with respect to the leaching time (days). This implies that despite the increasing leaching period, the presence of Pseudomonas (Sp.) did not consume the lead that is produced. The analysis as shown in Figure 13c also indicates that iron was decreasing with respect to the days of the leaching process as well as its cumulative % loss. It revealed that 25.25, 6.00 and 4.25 (in ppm) were dissolved for 7 days, 14 days and 21 days respectively in the cassava fluid extract. The cumulative % loss shows the progressive rate at which the iron is decreasing with respect to the leaching time (days). Hence, it also implies that reducing the leaching period gives better yield that prolong period which was due to the presence of Pseudomonas (Sp.) (Akcil et al. (2003)). The bacteria also consume the iron that should be produced. The Figure 13d shows the result for the copper obtained. It indicates that at 7 days, 14 days and 21 days; 3.75, 1.25 and 0.25 (in ppm) of copper was dissolved respectively in the leaves extract. Both the quantity of the copper obtained and the cumulative % loss show a similar trend with the zinc due to the same reason.

Table 4: Extraction of metals from the ore using cassava fluid extract by AAS

Period	Zn (ppm)	Pb (ppm)	Cu (ppm)	Fe (ppm)
7days	150.25	55.25	3.75	25.25
14days	149.50	62.25	1.25	6.00
21days	149.25	79.25	0.25	4.25

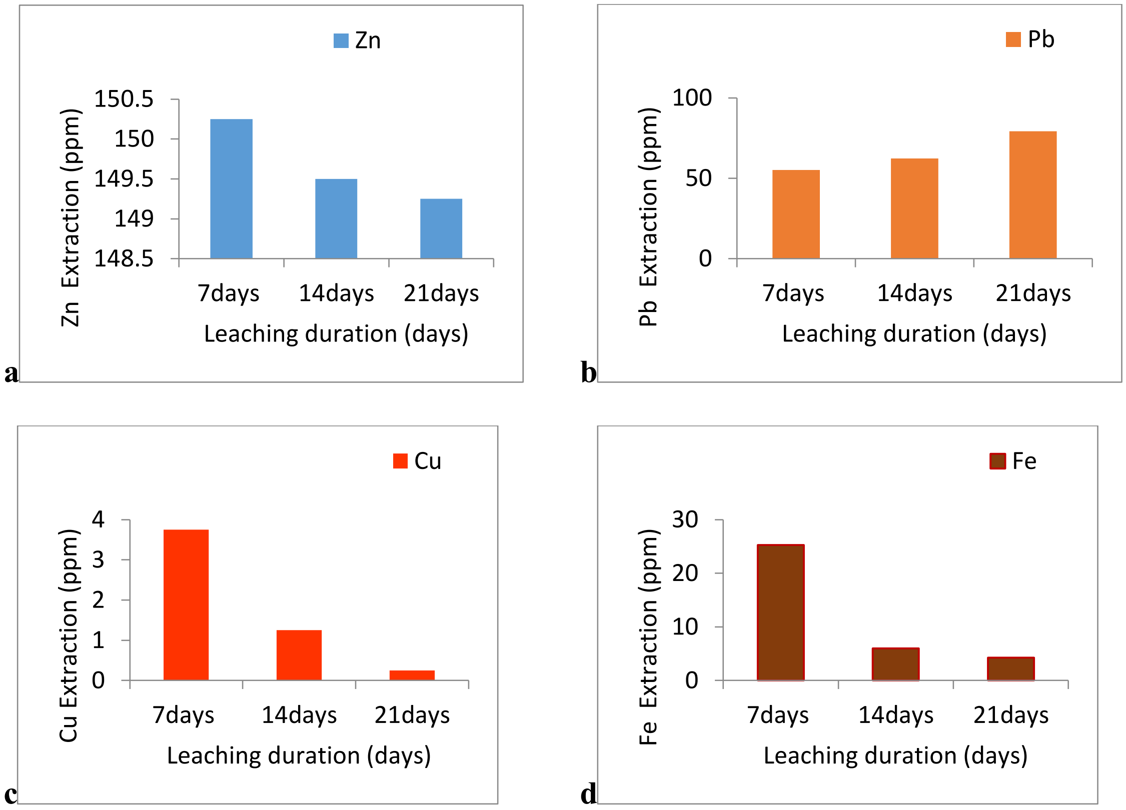


Figure 12: Result of metal extraction zinc ore using cassava fluid extract

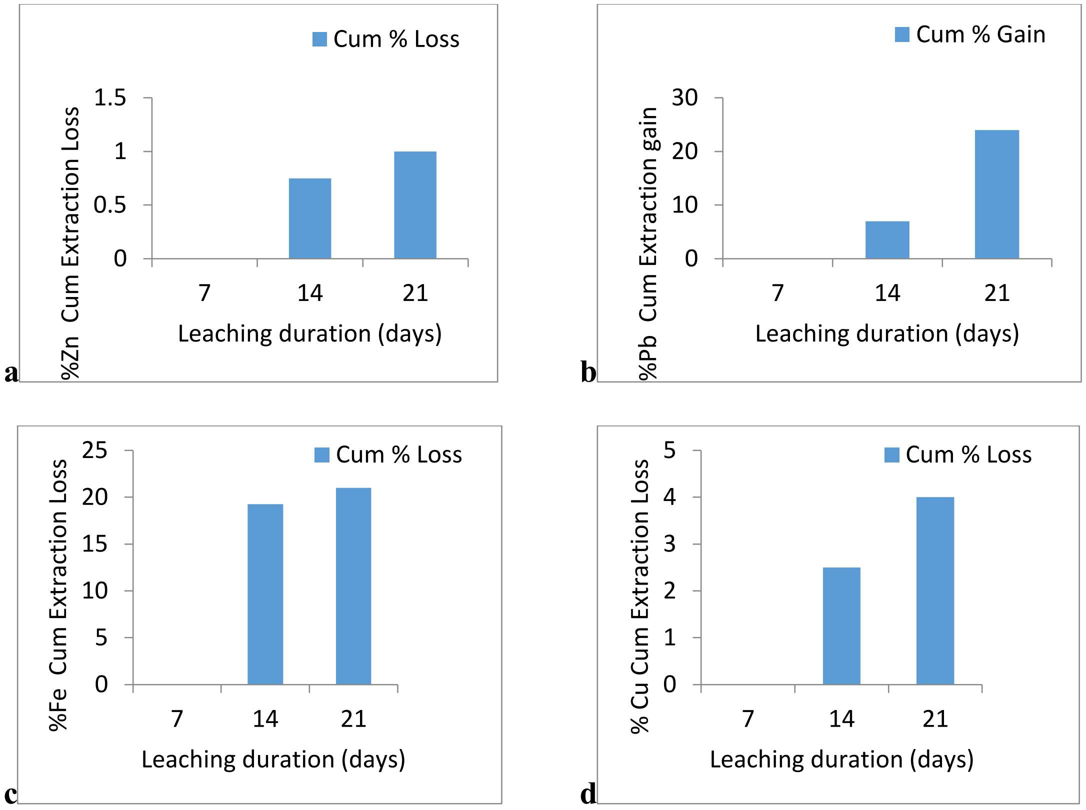


Figure 13: Metal extraction in cassava fluid with leaching time (days)

Assuming the normal range of cyanogen content between 15 mg and 400 mg hydrogen cyanide (HCN)/kg fresh weight; the series of possible chemical reactions speculated among some components such as ZnS, ZnO, PbO_2, PbO, due to hydrogen cyanide and water may be represented in equations [14-28] as:
For different compounds of zinc, reactions can be of the forms [14-19];

$ZnO + 2HCN \rightarrow Zn(CN)_2 + H_2O$ [14]

$3ZnO + 4HCN + H_2O \rightarrow 2Zn(CN)_2 + Zn(OH)_2 + H_2O_2$ [15]

$3ZnO + 4HCN + H_2O \rightarrow 2Zn(CN)_2 + Zn(OH)_2 + 2H_2O$ [16]

$ZnO + 2H_2O \rightarrow Zn(OH)_2 + H_2O$ [17]

$2ZnS + H_2O_2 \rightarrow ZnSO_4 + H_2O$ [18]

$ZnS + 3H_2O_2 \rightarrow ZnSO_3 + 3H_2O$ [19]

In the cases of lead sulphide and oxides [20-24];

$PbO_2 + 2HCN \rightarrow Pb(CN)_2 + H_2O_2$ [20]

$PbO + 2HCN \rightarrow Pb(CN)_2 + H_2O$ [21]

$PbS + 2H_2O_2 \rightarrow Pb(OH)_2 + H_2O$ [22]

$PbS + 3H_2O_2 \rightarrow Pb(OH)_2 + SO_2 + 2H_2O$ [23]

$Fe_3O_4 + 8HCN \rightarrow 3Fe(CN)_8 + 4H_2O$ [24]

For the (Fe,Zn)S and $CuFeS_2$ [25-28];

$(Fe,Zn)S + 2HCN + H_2O \rightarrow (Fe,Zn)(CN)_2 + (Fe, Zn)SO_4 + Zn(OH)_2$ [25]

$FeS + 2HCN + H_2O \rightarrow Fe(CN)_2 + FeSO_4 + Fe(OH)_2$ [26]

$ZnS + 2HCN + H_2O \rightarrow Zn(CN)_2 + ZnSO_4 + Zn(OH)_2$ [27]

$CuFeS_2 + 2HCN \rightarrow (Cu, Fe)(CN)_2 + (Cu, Fe)SO_4 + H_2O$ [28]

Since there is no anti metal consuming bacteria reagent added to the leaching system, long time (days) exposure of ZnO is not favourable to Zn extraction as obtained from the results. Thi may be due to the hydrolysis of the cyanogenic glycosides and subsequent elimination of the liberated HCN, the HCN content of cassava extract liquor reduced possibly by fermentation; thus there is reduction in amount of Zn, Fe and Cu as the leaching time (days) increased. As a remedy, meta-bromo-thiolactone (MBTL) could be added to reduce or make inactive the action of pseudomonas (Sp.) which consumes the cyanide content in the leachant (O'loughlin et al. (2013)).
The experimental results clearly revealed that the bioleaching extraction process produced less zinc and lead when compared

with the results obtained from the use of conventional acids and alkaline leaching previously reported by the author in the literature (Oluwaseyi and Egunlae (2007); Ajibola and Jimoh (2014); Ajibola et al. (2015)). Even though the bioleaching extraction process produced less zinc and lead at longer exposure time as compared with the use of acids and alkaline leaching reagents previously reported in the literature. However, much benefit can still be derived from bioleaching of ZnO; the abundant availability of cassava as natural resources, ease of processing and process operating at lower cost; and less environmental hazards and friendliness. With further research interest and studies; greater extraction yield is anticipated with the evolution of appropriate anti metal consuming bacteria reagents (inhibitors). The procedures of the bioleaching reactions, chemical stoichiometry and the detailed functions of the enzymes are yet to be fully understood; hence the need for further work in the area.

CONCLUSION AND RECOMMENDATION

From the result of the work carried out on the bioleaching of zinc using agro-cyanide extract, the itemized conclusions are drawn as follows:

a) The Nigeria complex sulphide ore is rich in Zinc, Pb, Ni, Cu, and many trace metals that can be explored for economic benefits.
b) Zinc sulphide was floated as concentrate and converted to ZnO by direct atmospheric roasting.
c) With the influence of biochemical agents, zinc and other associated metals such as lead, copper, and iron can be extracted using the cassava leaf extract as shown in the result of the Atomic Absorption Spectrometry (AAS) analysis.
d) The Zn dissolved in agro-cyanide at lower extraction rate than what was previously obtained from acid and alkaline leaching processes.
e) Long time (days) exposure of ZnO is not favourable to Zn extraction as obtained from the results. There is a reduction in the amount of Zn, Fe and Cu as the leaching time (days) increases. Further studies on the addition anti metal consuming bacteria reagents are necessary.
f) Even though the bioleaching extraction process produced less zinc and lead at longer exposure time as compared with the use of acids and alkaline leaching reagent previously reported in the literature; the process operates at lower cost and environmental hazards.
g) The bioleaching process should be adopted in the Zinc industry since the raw materials needed are largely valuable in the environment and it yields a better result by producing larger amounts of zinc and lead. The mechanisms of the leach reactions, stoichiometry and the roles of the enzymes are not fully comprehended; hence the need for further work in the area of increasing the Zn and Cu yields, thus reducing the consumption rate of these metals in the solution.

REFERENCES

Adepoju, O.T and Nwangwu, J.O (2010). Nutrient composition and contribution of noodles (*abacha*) and local salad from cassava *(Manihot spp)* to nutrient intake of Nigerian consumers. *African Journal of Food Science* Vol. 4, No7, pp. 422 – 426.

Ajibola O.O, Oloruntoba D.T and Owa A.F (2015). Leach-Electrowinning of Zinc from Abakaliki Complex Sulphide Ore. *Proceedings of Lead-Zinc Conference (Pb-Zn 2015) on Modern Processes and Future Development. Dusseldorf, Germany. Vol. 25, pp 561-575*.

Ajibola O.O and Jimoh B.O (2014). Agitation leaching recovery of lead and zinc from complex sulphide ore deposit using HF, HCl and H_2SO_4. *Advances in Applied Science Research*, 5(3), 68-72.

Akande S.O and Mucke A. (1989). Mineralogical, textural and paragenetic studies of the lead-zinc-copper mineralization in the lower Benue Trough (Nigeria) and their genetic implications. *Journal of African Earth Sciences (and the Middle East)*, Vol. 9, Iss. 1, pp 23-29. https://doi.org/10.1016/0899-5362(89)90004-3

Akcil A., Karahan A. G, Ciftci H, Sagdic O. (2003). Biological treatment of cyanide by natural isolated bacteria (pseudomonas sp.). *Minerals Engineering*. Vol. 16, No. 7, pp 643-649,

Barratt, N., Chitundu, D., Dover, O., Elsinga1, J., Eriksson, S., Guma, L., Haggblade, M., Haggblade, S., Henn, T.O., Locke, F.R., O'Donnell, C., Smith, C. and Stevens, T. (2006). Cassava as drought insurance: Food security implications of cassava trials in Central Zambia. *Agrekon,* Vol 45 No 1, pp 106-123.

Burstall F. H., Forrest P.J, Kember N.F, and Wells R.A. (1953). Ion exchange process for recovery of gold from cyanide solution, *Industrial & Engineering Chemistry* Vol. 45 (8), 1648-1658, DOI: 10.1021/ie50524a023

Cardoso A.P, Mirione E., Ernesto M., Massaza F., Cliff J., Haque M.R, Bradbury J.H, (2005). Processing of cassava roots to remove cyanogens, *Journal of Food Composition and Analysis* Vol.18, pp451–460

Ceballos, H., Iglesias, A.C, Perez, J.C and Dixon, A (2004). Cassava breeding: opportunities and challenges. *Plant. Mol. Biol*., Vol 56, No 2: pp 506–516.

Chávez, A.L., Sánchez, T., Jaramillo, G., Bedoya, J.M., Echeverry, J., Bolaños, E.A., Ceballos, H. and Iglesias, C.A (2005) Variation of quality traits in cassava roots evaluated in landraces and improved clones. *Euphytica,* Vol 143 No 27, pp125-133.

Chen A., Zhao Z. W., Jia X., Long S., Huo G., Chen X. (2009). Alkaline leaching Zn and its concomitant metals from refractory hemimorphite zinc oxide ore. *Hydrometallurgy*, Vol. 97, pp228–232.

Cun-Xiong L., Hong-Sheng X., Zhi-Gan D., Xing-Bin L., Ming-Tin L., Chang W. (2010). Pressure leaching of zinc silicate ore in sulfuric acid medium. *Transaction of Nonferrous Metals Society of China,* Vol. 20, pp918-923.

Egunlae and Jimoh B.O, (2010). Comparative effect of hydrogen peroxide and phenol as oxidants on the leaching of

Ilesa gold-silver ore using sodium cyanide as leachant. *Journal of Engineering and Earth Sciences* Vol. 4 No. 1, pp 54-57.

Egunlae O.O and Oluwaseyi A.O (2007). Leaching Ilesha gold-silver ore with NaCN, Thiourea And Agro-Cyanide under similar hydrometallurgical conditions. *Journal of Engineering and Earth Sciences*. Vol. 2 No. 1, pp 96-102.

Egunlae O.O, Adeloye A.O and Oloruntoba D.T (2006). Selective flotation of galena from Abakaliki lead-zinc sulphide ore using local plant oils. *Journal of Engineering and Earth Sciences,* Vol. 1 No. 1, pp 57-65.

Ejtemaei M., Irannajad M., Gharabaghi M. (2011). Influence of important factors on flotation of zinc oxide mineral using cationic, anionic and mixed (cationic/anionic) collectors. *Minerals Engineering*. DOI:24. 10.1016/j.mineng.2011.05.018.

Ejtemaei M., Irannajad M. (2008) Recovery of zinc oxide minerals from angooran mining tailings by flotation. MSc Thesis, Amirkabir University of Technology (Tehran Polytechnic), Iran.

Enidiok, S.E., Attah, L.E., Otuechere, C.A (2008). Evaluation of moisture, total cyanide and fiber contents of garri produced from cassava (*Manihot utilissima*) varieties obtained from awassa in Southern Ethiopia. *Pakistan Journal of Nutrition,* Vol 7, No 5, pp 625-629.

Espiari S., Rashchi F., Sadrnezhaad S. (2006). Hydrometallurgical treatment of tailings with high zinc content. *Hydrometallurgy,* Vol. 82, pp54–62.

He S., Wang J., Yan J., (2010) Pressure leaching of high silica Pb–Zn oxide ore in sulfuric acid me-dium. *Hydrometallurgy*, Vol.104, pp235–240.

Hershey, C., Henry, G., Best, R. and Iglesias, C. (1997). Cassava in Latin America and the Caribbean. *Cassava. Species*, Vol. 5, No 10, pp 426-427.

Irannajad M., Ejtemaei M., Gharabaghi M. (2009). The effect of reagents on selective flotation of smithsonite–calcite–quartz. *Minerals Engineering,* Vol. 22, pp 766–771.

Jimoh B.O and Egunlae O.O. (2010). Simulation of leaching parameters of NaOH and H_2SO_4 for large scale extraction using V-Basic. *Proceedings of 6th Engineering Forum*, Vol. 6(1): pp123-126.

Ju S., Motang T., Shenghai Y., Yingnian L. (2005) Dissolution kinetics of smithsonite ore in ammonium chloride solution. *Hydrometallurgy*, Vol.80, pp67–74.

Meshkini M., Irannajad M., Azadmehr A., Abasi Rohallahi A. (2011). Extraction of Zinc from Low Grade Zinc Oxide Ores using Bacteria. *Second National Conference of Applied Microbiology*. Tehran, Iran.

Mousavi SM, Jafari A, Yaghmaei S, Vossoughi M, Turunen I. (2009). Experiments and CFD simulation of ferrous biooxidation in a bubble column bioreactor. *Process Biochemistry Journal. Vol.* 44, pp696–703.

Nwoke M.A.U (1997). Application of some Nigerian plant oils as fatty acid collectors for recovery of baryte from tailing at Azara. *Nigerian Mining Journal* Vol.2 (1) pp42-55

O'loughlin C.T, Miller L.C, Siryaporn A, Drescher K, Semmelhack M.F, Bassler B.L (2013). A quorum-sensing inhibitor blocks pseudomonas aeruginosa virulence and biofilm formation, 1798, 1-6.

Obarezi J. E. and Nwosu J. I. (2013). Structural controls of Pb-Zn mineralization of Enyigba district, Abakaliki, Southeastern Nigeria. *Journal of Geology and Mining Research,* Vol. 5(11), pp 250-261, DOI: 10.5897//JGMR13.0189

Okafor E.G. and Uwadiale G.G.O.O, (1997). Process mineralogy of the Ishiagu lead-zinc deposit, Nigeria. *Mining, Metallurgy & Exploration*, Vol.14, pp 45-48. Doi:10.1007/BF03402778

Oluwaseyi A.O and Egunlae O.O (2007) Alkaline leaching characteristics of Nigerian lead-zinc sulphide ore. *Journal of Engineering and Earth Sciences* Vol. 2(1): pp6-11.

Onal G., Bulut G., Gul A., Kangal O., Perek K., Arslan F. (2005) Flotation of Aladag oxide lead–zinc ores. *Minerals Engineering,* Vol.18, pp279–282.

Onyemaobi O.O (1990) Evaluation of flotation performance of Nigeria's (ZnS) sphalerite w/o action by copper, *Ife Journal of Technology*, Vol 2, No 2, pp 21-25

Razanamahandry L.C., Karoui H., Andrianisa H. A., Yacouba, H. (2017). Bioremediation of soil and water polluted by cyanide: A review. *African Journal of Environmental Science and Technology*, Vol. 11(6), pp272-291.

Souza A.D, Pina P.S, Lea˜o V.A. (2007) Bioleaching and chemical leaching as an integrated process in the zinc industry. *Minerals Engineering Journal* Vol.20: pp591–599.

Svens K, Kerstiens K, Runkel M. 2003. Recent experiences with modern zinc processing technology. *Erzmetall* 56: 94–103.

Victor O.M, Onwuemesi A.G, Aniwetalu, Emmanuel U. (2015) Exploration of lead-zinc (pb-zn) mineralization using very low frequency electromagnetic (VLF-EM) in Ishiagu, Ebonyi State. *Journal of Geology and Geosciences.* Vol. 4: 214. Doi:10.4172/2329-6755.1000214

Wilson W. and Dufour D. (2006). Ethnobotanical evidence for cultivar selection among the Tukanoans: Manioc (*Manihot esculenta Crantz*) in the Northwest Amazon. *Culture and Agriculture*. 28. 122-130. 10.1525/cag.2006.28.2.122.

Xu H., Wei C., Li C., Fan G., Deng Z., Li M., Li X. (2010) Sulfuric acid leaching of zinc silicate ore under pressure.

Hydrometallurgy, Vol.105, pp186–190.

Zhao Youcai, R. Stanforth, (2000). Extraction of zinc from zinc ferrites by fusion with caustic soda. *Minerals Engineering*, Vol. 13, Iss 13, pp 1417-1421

APPENDIX

Table A1: Calculation of extraction of element from ore

Leaching time	Extraction	Loss	Cumulative (loss or gain)
7days	a_1	$b_1 = 0$	$c_1 = 100 - b_1$
14days	b_2	$b_2 = a_2 - a_1$	$c_2 = 100 - (b_1 + b_2)$
21days	c_3	$b_3 = a_3 - a_2$	$c_3 = 100 - (b_1 + b_2 + b_3)$

Table A2: Result of extraction of Zn from ore using cassava fluid extract

Leaching time (days)	Zinc (ppm)	Loss (ppm)	Cumulative loss
7	150.25	0	0
14	149.50	0.75	0.75
21	149.25	0.25	1.00

Table A3: Result of extraction of Pb from ore using cassava fluid extract

Leaching time (days)	Lead (ppm)	Gain (ppm)	Cumulative gain
7	55.25	0	0
14	62.25	7.00	7
21	79.25	17.00	24

Table A4: Result of extraction of Fe from ore using cassava fluid extract

Leaching time (days)	Iron (ppm)	Loss (ppm)	Cumulative loss
7	25.25	0	0
14	6.00	19.25	19.25
21	4.25	1.75	21

Table A5: Result of extraction of Cu from ore using cassava fluid extract

Leaching time (days)	Copper (ppm)	Loss (ppm)	Cumulative loss
7	3.75	0	0
14	1.25	2.50	2.5
21	0.25	1.50	4