# Effects of Collectors Produced from Selected Tropical Plants on the Recovery of Galena Concentrate

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**Abstract**

This research work studied the performance of collectors produced from corn oil, olive oil, soya beans and palm oils on the flotation of Ishiagu sulphide ore. The sulphide ore was comminuted and subjected to particle size analysis using the following particle sizes: 212µm, 150µm, 105µm, 75µm, 63µm and -63µm. The chemical analysis of the ore was carried out to determine the minerals present expressed in part per million (ppm). Collectors were prepared from the addition of potassium and sodium hydroxide solution in accordance with ASTM D543. The natural oils of the selected plants were used as frothers. In accordance with ISO 23499:2008 froth flotation experiments were carried out on the samples of different fractions using the locally prepared collectors from corn, olive, soya bean and palm oils. Flotation parameters used were pulp pH values of 9.00, 9.50, 10.00, 10.50 and 11.00; collector concentrations of 100mg/l, 200mg/l, 300mg/l, 400mg/l 500mg/l and 600mg/l and pulp densities of 10 g/l 20 g /l, 30g /l, 40g /l, 50g /l and 60g /l. Collector produced from corn oil in sodium hydroxide at particle size range of -105 +75µm gave the highest recovery of 93.24% for galena concentrate, while that of corn oil in potassium hydroxide gave highest recovery of 82.97% at the same particle size range for the galena concentrate. pH of 10.5 gave the highest recovery of 85.81% with corn oil in potassium hydroxide solution as the collector. Pulp density of 50g/l gave the highest recovery of 88.74% with corn oil in potassium hydroxide solution as the collector and collector concentrations 600mg/l gave the highest recovery of 90.99% also with corn oil in potassium hydroxide solution as the collector. Hence, optimum conditions of -105µm +75µm, pH of 10.5, pulp density of 50g/l and collector concentrations of 600mg/l is found suitable for the recovery of galena concentrate from the Ishiagu complex sulphide ore. Therefore, collectors and frothers produced from corn oil in potassium and sodium hydroxide are possible substitutes for the imported ones.

**Keywords**

Collectors, Frothers, Concentrates and Recovery.

## 1 Introduction

Nigeria is blessed with many natural resources, particularly industrial and metaliferous minerals. The available minerals resources in Nigeria range from industrial mineral like asbestos, barites, bentonite, limestone, clay, feldspar, graphite, gypsum talc, salt, quarts, phosphate, mica to metaliferous ore like iron ore, cassiterite, columbite, lead – zinc ore and Ferro-alloy deposits found in different locations in Nigeria (Aso and Ajayi, 1999). An ore can be described as an accumulation of minerals in a sufficient quantity as to be capable of economic extraction (Wills, 2006). Galena – sphalerite ore reserve at Abakaliki in Eastern Part of Nigeria is valued at about 15 million tons (Onyemaobi, 1990). This means that the reserve is economically viable. Minerals by definition are natural inorganic substance possessing definite chemical composition and atomic structures (Wills, 2006). The forms in which metals are found in the earth crust depend on their reactivity with the environment particularly with oxygen, sulphur, and carbon dioxide, Gold and platinum metal ore found principally native or metallic form. Silver, copper and mercury are found native as well as in the form of sulphides, carbonates and chlorides. The more reactive metals are always in the compound form such as the oxides and sulphides or iron and oxides of aluminium and beryllium. The naturally occurring compounds are known as minerals, most of which have been given names according to their compound (Wills, 2006). Examples of these compounds are galena, lead sulphide, Pbs: sphalerite, Zns and Pyrite $FeS_2$. Metals are highly useful as they are the backbone of all engineering projects and products. Their uses vary from primitive tools of agriculture to advance aircrafts, automobiles, building and bridge construction, railways, light and heavy machinery and equipments shipping and transportation. Lead-Zinc multimetal sulphide ores are important non-ferrous mineral throughout the world. The Romans used Lead extensively particularly for waters pipes, soldered with an alloy of lead and tin (Tony and Bob 2008).

The sulphide ore cannot be conveyed to the smelting plant for the production of lead metal except it first passes through mineral processing route in order to remove the gangues associated with it. This is done to improve the grade of the ore and to reduce the bulk of the ore to be transported and processed by the smelter. Froth flotation is the concentration method that is gainfully employed for the processing of the sulphide ore. The fact that flotation reagent especially collectors and frothers are very scarce and expensive in Nigeria is the reason for this study which aimed at the possibility of exploring locally derived substitutes.

**Geology of the Deposit**

Ishiagu is in the eastern part of Nigeria, located between latitude N65-80W and longitude N10-15W. The ores in the deposit are hosted by closely jointed shale of Asu river group of only sedimentary rock of lower cretaceous age (Orajaka, 1965). The sedimentary rocks are predominantly black carbonaceous shale with occasional inclusions of thin calcareous matter (Ladkpe, 1998). The Lead-Zinc lodes are among the largest base metal deposit within the lower cretaceous sedimentary sequence of the Benue structure. It was ascertained that there are up to nine lodes which make up the deposit; namely Ishiagu, Eyimba, Ameri, Isu, Ikwo, Palm wine, Nine pence and portugese lodes. The microscopic studies on Ishiagu lead-zinc ore showed that galena and sphalerite are the major economic compounds in the ore. Gangue which are pyrite ($Fes_2$), Azunite [$sCUCO_3$ $CuOH_2$, and quart $(SI)_2$), are ore (Akande *et al*, 1990, Oyemaobi, 1990 *;* Orajaka 1965) observed that galena in the lodes appears to be of two generation relative to their crystallization pattern. Orazulike (1994) was of the opinion that galena in its lodes appeared to be of their types according to their shapes, namely cubic, fibrous and granular.

**Major Ores and Minerals**

Lead rarely occurs as a native metal in nature. The main lead ore mineral is galena, which may contain minor amounts of silver. Galena oxidizes to various secondary lead mineral, mainly cerrusite, anglesite and pyromorphite $Pb_5(PO)_3CI$.The chief mineral is sphalerite, which commonly contains iron up to a maximum of about 36%, and small to trace quantities of managanese and cadmium. In a few deposits, frankline (Zn,Mn,Fe) $(Fe,Mn)_2)_4$ and willemite ZnSi)4 are the principal ore minerals. The main secondary zinc minerals are smithsonite and hemimorphite $(ZnOH)_2SiO_3$.

Lead and zinc ores generally occur together, usually with silver. Most of the world production of arsenic, antimony and bismuth is a byproduct from lead and zinc ore. Ores of lead and zinc are mostly in the range of 3 to 20 wt to 20 wt % of either or both metals, but grades are, more commonly 5-15% with averages.

**Properties of Lead**

Lead, a member of group IV of the periodic table, is a dense, bluish-grey metal that is soft, malleable and ductile. It has low tensile strength and is a poor conductor of electricity. When freshly cut the surface oxidizes to a dull grey coating made up of a mixture of lead and lead monoxide, which protects the metal from further corrosion. Lead and many of its compounds are toxic when taken internally. Continuous exposure to even low levels of lead can be dangerous, particularly for growing children causing impairment of their mental and physical development.

**Uses of Lead**

Lead is the fifth most used metal after iron, aluminium, copper and zinc. Lead is used mainly for storage batteries, sheathing electric cables, construction (e.g. roof flashings), lining pipes and tanks in industry and in ammunition (shot and bullets). Lead sheets are used in buildings to absorb sound. Because it effectively absorbs electromagnetic radiation at short wavelengths, lead is used as a protective shielding in X-ray and radioactive applications. It is used in numerous alloys such as brass (Cu and Zn) and bronze (Cu and Sn). Alloys containing a high percentage of Lead include: solder (Pb = Sn), type metal (commonly 58%, Pb, 26% Sn, 15% Sb, 1% Cu), Britannia metal (Pb-Sb-Cu), pewter (Sn-Sb with historically about 25% Pb) and various bearing metals (10-90% with Sn, Sb, and Cu). Compounds of lead are used in antiknock additives for petrol to prevent premature detonation in internal-combustion engines (tetraethyl lead $Pb(C_2H_5)_4$, and in paints and pigments (e.g. white lead $PbCO_3)_2$ $Pb(OH)_2$, $Pb(OH)_2$, liithage PbO, red lead Pb304 and chrome yellow $PbCrO_4$).

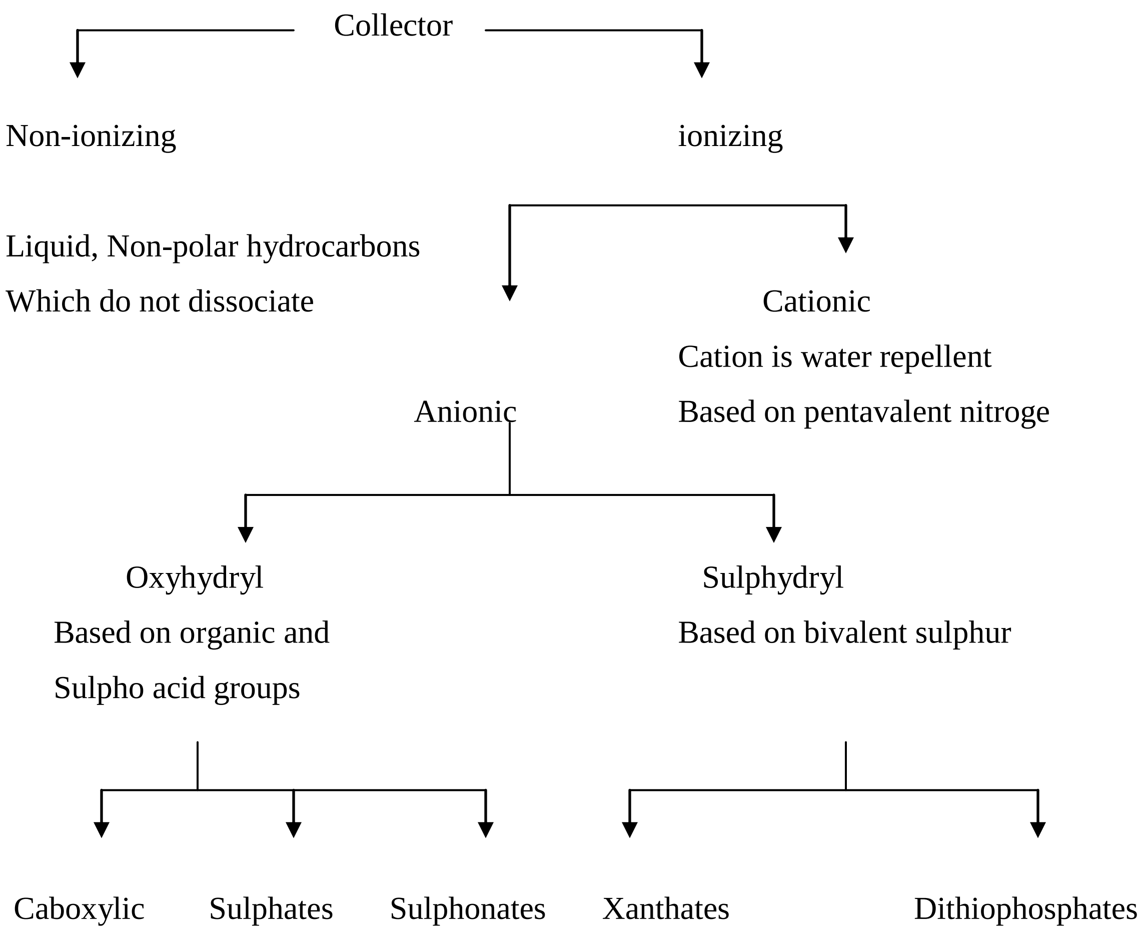
Froth flotation is an extractive process where various minerals can be selectively extracted. Jowett (1975) define froth flotation as a means of achieving solid-waste separation in a liquid medium, through mutations of the process are also used to effect solid-liquid separation (dissolved air flotation) and liquid-separation (foam fractionation). Finch and Smith (1979) observed that froth flotation is a versatile mineral processing technique which utilizes difference between the physico-chemical surface properties of a mineral. Meanwhile, according to Wills

(2006), froth flotation is a selective process and can be used to achieve specific separation from complex ores such as lead-zinc, copper-zinc. Froth flotation is known to be the most important method of concentration (Adewuyi and Opafunso, 2002). Separation by flotation is based on the ability or lack of ability of different surfaces to be wetted by water. The wettability of a surface is determined by the relative values of the interfacial energies: solid-water, solid-air, and water-air. If the first of these is large compared to the other two, water will not cling to the solid, and the solid is said to be hydrophobic (fear of water). Conversely if the solid-air interface energy is the larger, the surface is said to be hydrophilic (love for water) and is easily wetted. In flotation processes air is blown through the aqueous pulp of ground ore. Those minerals which are hydrophobic will cling to the air bubbles and rise with them, whereas the hydrophilic minerals will sink. In order to carry out flotation successfully various additions have to be made to the pulp, via: - collectors, frothers, activators, depressants, and conditioners. The reagents for froth flotation are not easy to come by in Nigeria and where available they are expensive especially the two major ones (i.e. collectors and frothers). The fact that flotation reagent especially collectors are very scarce and expensive in Nigeria is the reason for this study and the results reveal the possibility of preparing the collectors locally to be used as substitutes for the imported ready-made.

**Froth Flotation**

Froth flotation commences by comminution (that is, crushing and grinding), which is used to increase the surface area of the ore for subsequent processing and break the rocks into the desired mineral and gangue in a process known as liberation, which then has to be separated from the desired mineral (Wills, 2006). Two major flotation reagents are collectors and frothers. Collectors are organic compound which render which render minerals water repellent by adsorption of hydrophobic molecules or ions on the mineral surface. It has been discovered that they act by forming the equivalent of a very thin oily layer on the mineral surface, which the air bubbles attaches itself to (Jowett, 1975). The addition of frothers which are surface active organic compounds, make a stable froth to be formed. The stable froth may be skimmed off together with the floated particles. The main factors that affect the floatability of any frother include the chemical structure of frother interaction between collector and frother, collector dosage, frother dosage, dispersion of frothers, water quality, flotation equipment system and structure and surface properties of particles (Yunkai et al, 2002). There are three main types of frothers they are: alcohols alkoxyparaffins and the polyglycol ethers. The commonly available commercial frothers are pine oil, eucalyptus oil, Methyl Isobuty Carbinol (MIBC), cresylic acids etc. Pine oil, (Ca turpentine fraction) and higher alcohols is typical flotation frother**.** (Crozier and Ottley, 1978; Crozier and Klimpel, 1985; Hansen and Klimpel, 1987; Laskowski, 1993).

The ore to be treated is first ground into a fine powder and the desired mineral is rendered hydrophobic by the addition of the collectors. The particular chemical depends on which mineral is to be collected as concentrate. The pulp of hydrophobic mineral-bearing ore and the unwanted part (gangue) being hydrophilic is then aerated, creating bubbles. The hydrophobic grains of mineral-bearing ore escape the water by attaching to the air bubbles, forming froth which could be stiffened by the addition of certain oils called frothers. The froth is removed and the concentrated mineral is collected for further refining. Fig. 1.0 reveals the classification of collectors after Glemboltskii *et al* 1972.



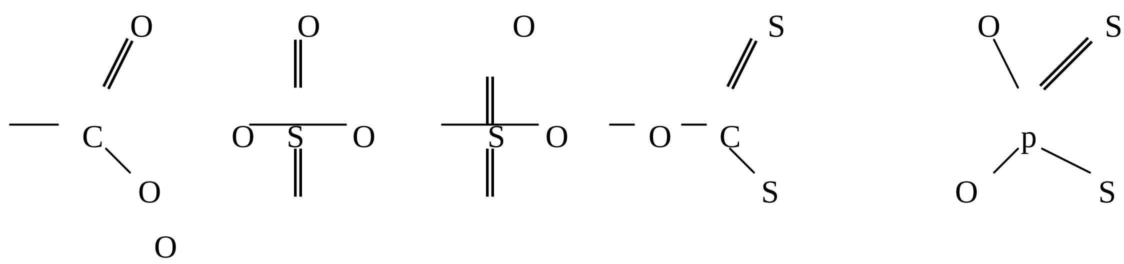



**Fig. 1.0 Classification of Collectors (Glemboltskii *et al* (1972).**

## 2 Materials and Methods

Sulphide ore obtained from Ishiagu, in Ebonyi state, Nigeria was used for this study. Groundnut oil, olive oil, soya beans and palm oils processed locally were also procured as well as Sodium Hydroxide (NaOH) and Potassium Hydroxide (KOH) pellets. The equipment used are Denver laboratory ball mill, Endecott's sieves set, Denver D-12 flotation cell and Atomic Absorption Spectrometer. The pebbles of the ore were reduced using the Denver laboratory ball mill. Sieve analysis was carried out on the pulverized ore using 212µm, 150µm, 105µm, 75µm, 63µm and -63µm sieve sizes in accordance with British Standard, B.S 410:1976. Chemical analysis was then performed on the pulverized ore to determine elemental composition in parts per million (ppm) which is in accordance with standard procedure in ASTM (2003) – C114.

In accordance with standard procedure in ASTM D543 2.5M of NaOH and KOH solutions were prepared by dissolving 100g of NaOH and 140g of KOH salt respectively in 1 $dm^3$ of distilled water. 50ml of 2.5M of each of NaOH and KOH were added to 50g of each of the oils in separate containers, stirred and heated together in a water bath until homogenous mixture were formed. Each of the homogenous mixtures served as collectors with its oil as frother for the flotation experiment.

The froth flotation experiments were performed using the Denver D-12 flotation cell in accordance with International Standard for Froth Flotation Business Government and Society, ISO 23499:2008.

Experiments were also performed to evaluate the influence of the flotation parameters (particle size, pulp pH, pulp density and collector concentration) on the recovery of galena from sulphide ore. The concentrates collected were also analysed and the effects of the various parameters on the recoveries of galena concentrates from the sulphide ore are presented in figs. 4-7.

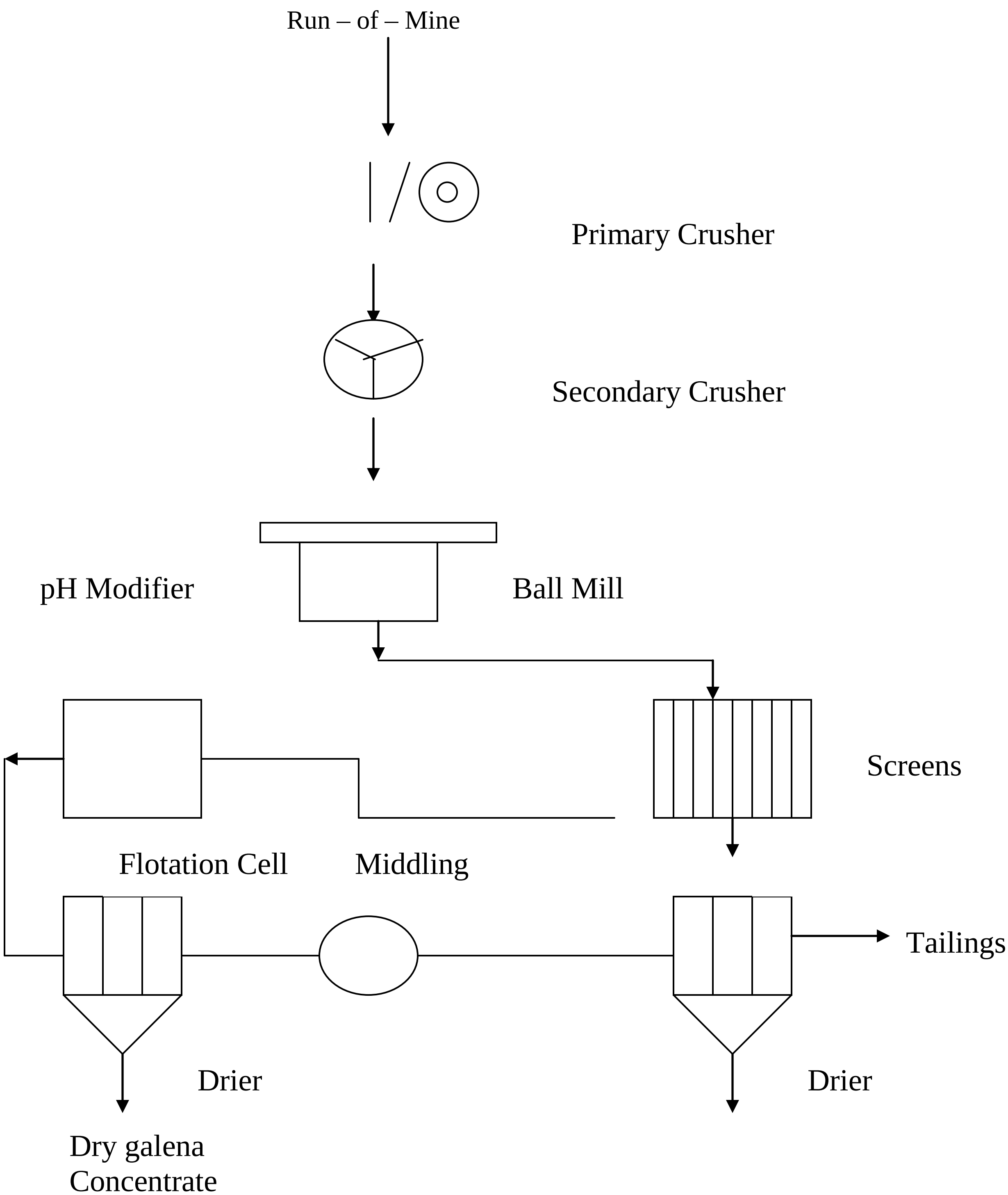



**Fig. 2.0The flow sheet of recovery of galena concentrates by froth flotation**

## 3 Results

**Table 1.0 The result of the pre-flotation analysis in part per million (ppm)**

| Fraction (µm) | Pb | Zn | Ca | Na | Fe | Cu | Si | Cd | As |
|---|---|---|---|---|---|---|---|---|---|
| +212 | 10.42 | 3.40 | 0.43 | 1.85 | 8.13 | 5.52 | 0.20 | 6.70 | 0.42 |
| -212 + 150 | 10.65 | 3.35 | 0.50 | 2.57 | 8.40 | 4.02 | 0.21 | 7.60 | 0.45 |
| -150 + 105 | 10.30 | 3.62 | 0.50 | 2.62 | 10.20 | 4.30 | 0.30 | 8.61 | 0.45 |
| -105 +75 | 11.25 | 3.38 | 0.50 | 2.70 | 8.08 | 3.75 | 0.28 | 8.45 | 0.45 |
| -75 +63 | 10.65 | 3.15 | 0.79 | 2.91 | 9.82 | 6.78 | 0.37 | 8.55 | 0.73 |
| -63 | 10.70 | 3.92 | 0.55 | 2.55 | 8.43 | 5.57 | 0.30 | 7.82 | 0.65 |

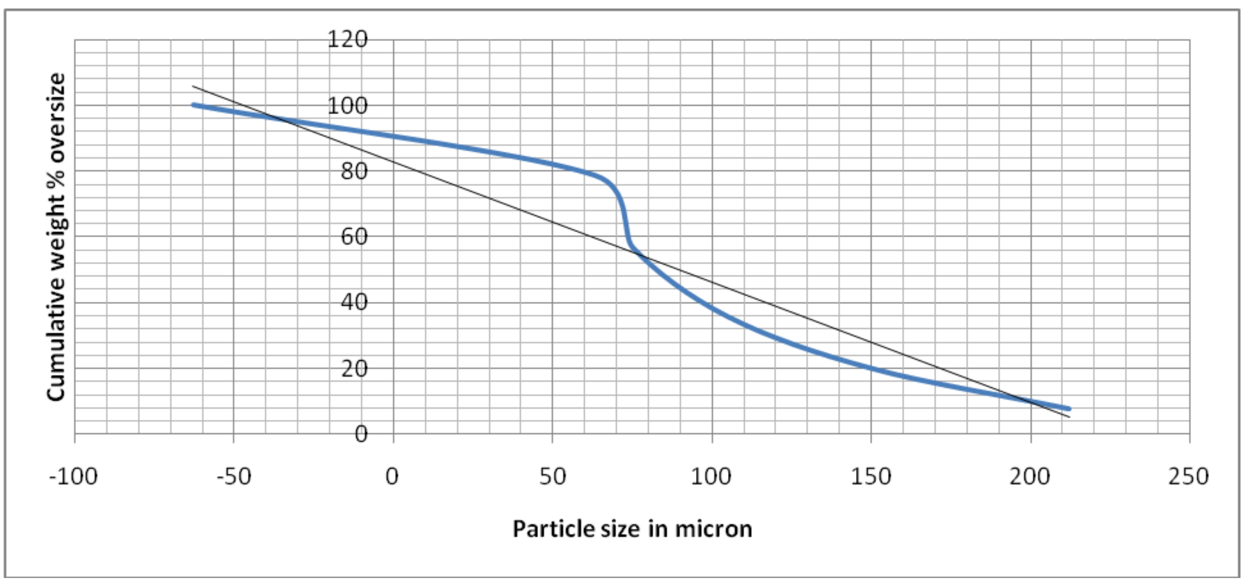



**Fig. 3.0 Graph of cumulative % oversize versus particle size**

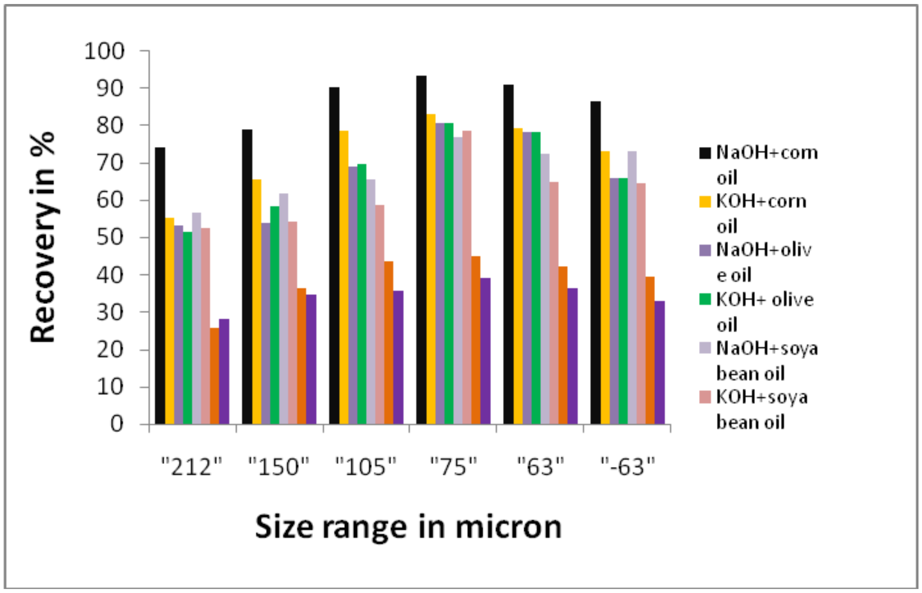



**Fig. 4.0 Graph of Size Range versus Recovery**

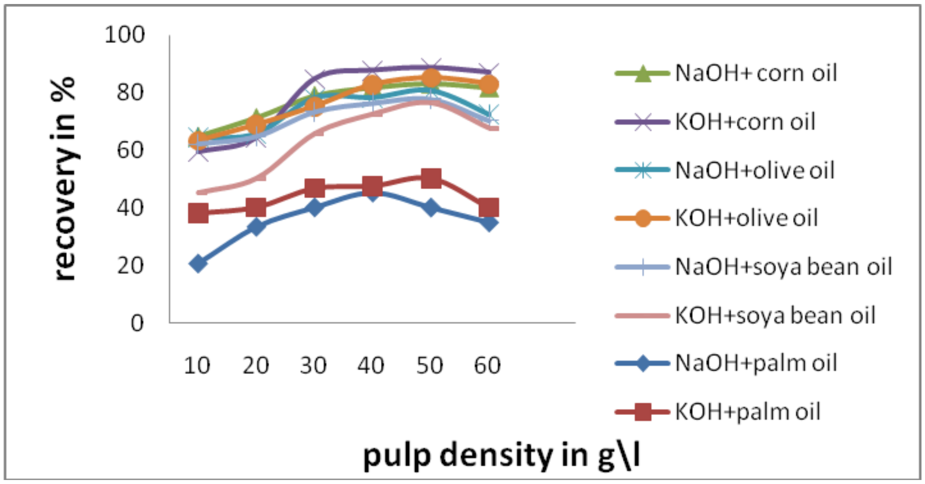



**Fig. 5.0 Graph of Pulp Density versus Recovery**

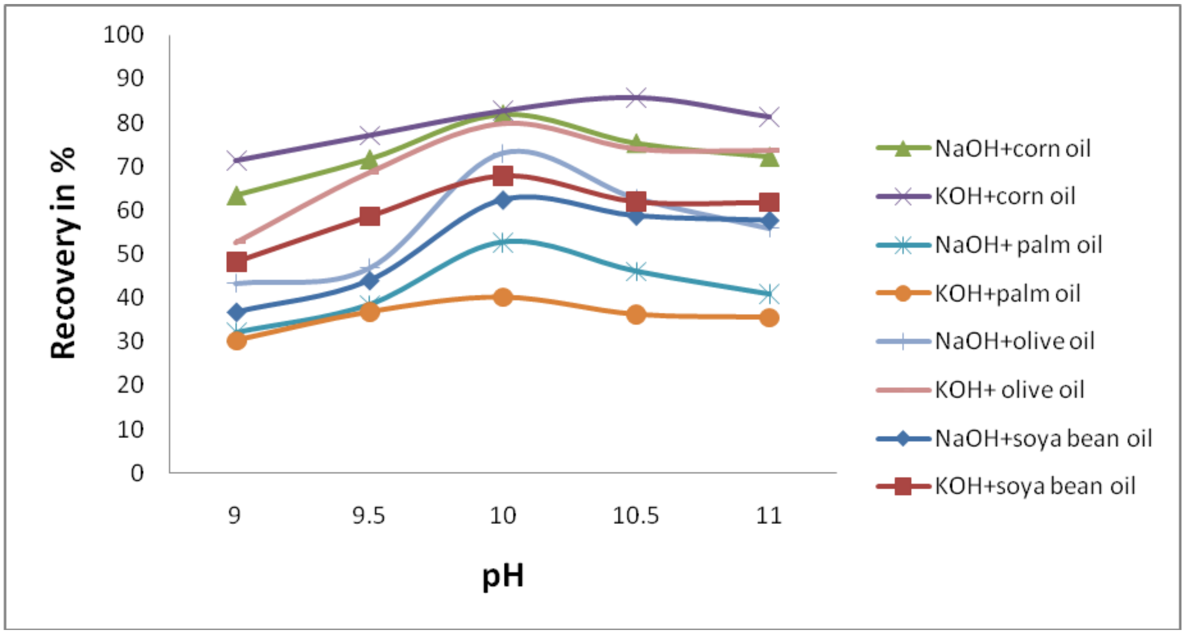



**Fig. 6.0 Graph of pH Versus Recovery**

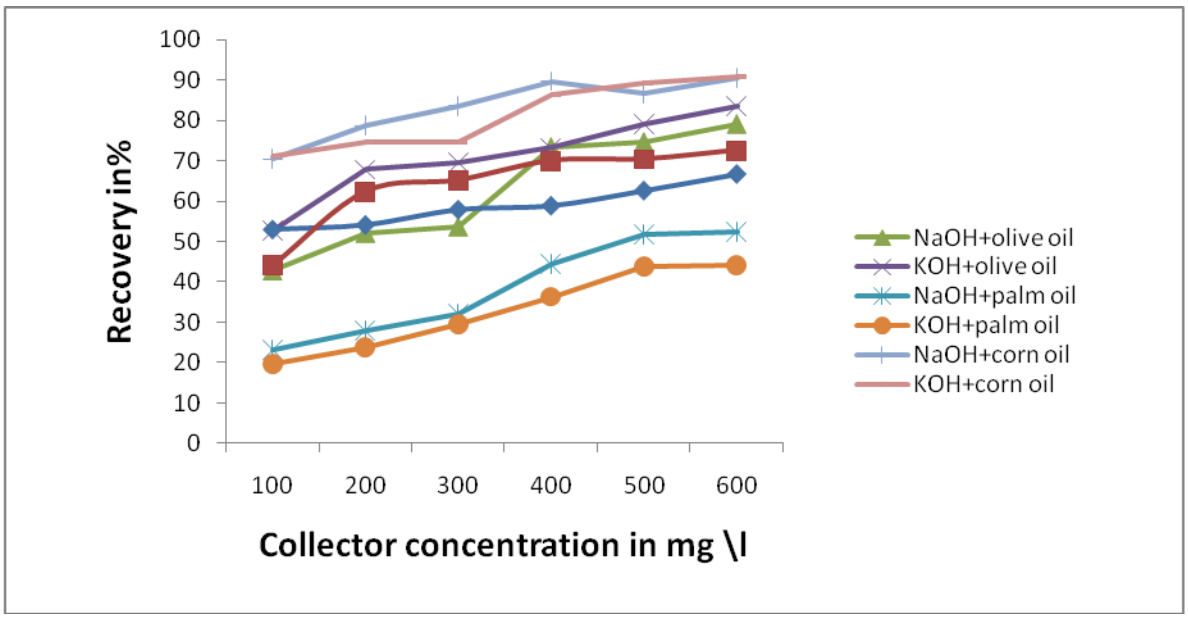



**Fig.7.0 Graph of Collector Concentration versus Recovery**

## 4 Discussions

The result of the particle size analysis revealed that for more fines to be produced from the ball mill more energy is required to mill the oversize. A high degree may only be possible by intensive fine grinding which may reduce to such a fine size that separation becomes inefficient. Froth flotation requires more valuable mineral surface to be exposed (Wills, 2006).

Collector molecules may be ionizing compound which dissociate in ions in water or non ionizing compound which are practically in soluble thereby rendering the mineral hydrophobic by covering its surface with a thin film. The surface of the mineral is separated is separated from the air bubbles to such a level that attachment of the particle can be made on contact. Two hypothesis put forward are chemical reaction hypothesis and the adsorption hypothesis by Taggard and others, that is collection in mineral is due to chemical reaction and may be simplified thus:

$$MA + X \longrightarrow MX + A \quad \text{------------------------ Equation 1}$$

Where M is the metal in the Minerals

A is the iron in the Minerals and

X the collector anion

By the adsorption hypothesis, all ions dissolve sin floatable pulp liquor adsorb at the mineral surfaces. The adsorption is specific and depends on the concentration of the dissolved ion under consideration. When sufficient collector has been adsorbed, then the mineral is floatable.

The frothers are oils while the collectors are soapy when bubbles are formed the frothing action is due to the ability of the frother to adsorb on the air – water interface because of its surface activities and to reduce the surface tension, thus stabilizing the air bubbles

**Pre- Flotation Analysis of Ishiagu Lead Ore**.

Lead, Pb; Zinc, Zn; Calcium, Ca; Sodium, Na; Iron, Fe; Copper, Cu; Silicon, Si; Cadmium, Cd; Arsenic, As are some of the element present in the run-of-mine. Lead is the element with highest value of 11.25 in part per million (ppm). The result shows that the elemental composition of the ore varies at different particle sizes. The highest value of lead was at "-105+75"microns with amount being 11.25 in Part Per Million (ppm).

**Effect of particle size**

Particle size 75 µm gave the highest value of recovery which was obtained from corn oil in sodium hydroxide that is 93.24%. This was followed by olive oil in potassium hydroxide which was 80.54%. Recoveries at coarser particle sizes were low and the increases as the sizes reduce up to 75 µm which was the highest after they became low again. This is in conformity with the findings of Gilchrist (1989) that coarser materials are generally heavy to be carried out of the pulp by the air bubbles. Slimes are also difficult to collect because they fail to enter air bubbles. Runge K.C *et al* (2003) in their findings documented that particles sizes affects flotation recovery rate, which not all particles of a particular size float with the same rate and that flotation separation is based on the fact that different mineralogical species exhibit different degrees.

This also agrees with stokes law:

$$V = gd^2\frac{(Ds - Df)}{18\eta} \quad \text{-------------------------- Equation 2}$$

d is the diameter of the particle

Ds is the density of solid falling under gravity in Df, density of fluid. η is the fluid viscosity; V is the terminal velocity while g is the acceleration due to gravity.

**Effect of Pulp Density on the Recovery**

The pulp density investigated were 10g/l, 20g/l, 30g/l, 40g/l, 50g/l and 60g/l. 88.74% It was also observed that the recovery increases gradually with increase in pulp density up to 50g/l and then drops at 60g/l for all the samples. This conforms to the fact that in froth flotation pulps can be as low as 8% and as high as 55% (Wills, 2006)

**Effect of Pulp pH on the Recovery**

Fig.6.0 shows the effect of pulp pH on the recovery of galena concentrate. Highest recovery was 85.81% obtained from corn oil in potassium hydroxide which was given by pH of 10.5 at the predetermined particle size of 75µm. Ideally, sufficient alkali will depress almost any sulphide mineral and there is always a critical pH values below which any given mineral will not float. This value depends on the nature of the mineral the particular collector and its concentration, and the temperature (Sultherland and Wark, 1955). Meanwhile at pH of 11.00 the value of recovery became low.

### Effect of Collector Concentration on the Recovery

The collector concentration investigated were 100mg/l, 200mg/l, 300mg/l, 400mg/l, 500mg/l and 600mg/l. It was observed that the recovery increases with increase in collector concentration, the highest being 90.99% which was obtained from corn oil in potassium hydroxide with other parameters kept constant. Fig.7.0. Also, 83.4% was obtained for olive oil in potassium hydroxide, 79.14% for olive oil in sodium hydroxide 72.64% for soya beans in potassium hydroxide, 66.66% for soya bean in sodium hydroxide while 44.24% and 52.54% are for palm oil in potassium hydroxide and sodium hydroxide respectively. This implies that corn oil in potassium hydroxide gave the best result while that of palm oil was not satisfactory.

## 5 Conclusion

It is ascertained that collectors and frothers produced from corn oil in sodium and potassium hydroxide are possible substitutes for the imported ones when compared with previous work carried out with use of ready-made reagents (collectors and frothers) . Collector produced from corn oil in sodium hydroxide at particle size of 75µm gave the highest recovery of 93.24% for galena concentrate, while that of corn oil in potassium hydroxide gave highest recovery of 82.97% at the same particle size range for the galena concentrate. pH of 10.5 gave the highest recovery of 85.81% with corn oil in potassium hydroxide solution as the collector. Pulp density of 50g/l gave the highest recovery of 88.74% with corn oil in potassium hydroxide solution as the collector and collector concentrations 600mg/l gave the highest recovery of 90.99% also with corn oil in potassium hydroxide solution as the collector. Thus, the optimum conditions for the recovery of galena concentrate from the bulk of Ishiagu sulphide ore are; particle size of 75µm, collectors derived from corn oil in sodium and potassium hydroxide and the natural oil as frother, collector concentration of 600mg/l, pH of 10.5 and pulp density of 50g/l.

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