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# Study of the Eco-Friendly Chemical Leaching of Cassiterite Ore Obtained from Du, Jos

South, Plateau State, Nigeria in Acidic Media for Tin Extraction

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### Abstract

The present era is witnessing a steady increase in demand for tin metal due to their use as critical components in the telecommunication, economic and industrial fabric of every nation. Many developing countries are diversifying their economies particularly to solid mineral development; through utilization of modern metal extraction technologies that are not only eco-friendly but also lead to extraction of high percentage of tin metal with high degree of purity. In this study, chemical leaching of cassiterite ore mined from Du community in Jos South, Plateaus State, Nigeria has been investigated. The significant mineral composition of the ore was determined by Inductively Coupled Plasma- Graphite Furnace Atomizer to be: 60.98% SnO<sub>2</sub>, 8.70% SiO<sub>2</sub>, 5.70% ZrO<sub>2</sub>, 5.56% Fe<sub>2</sub>O<sub>3</sub>, 4.81% NbO, 4.07% TiO<sub>2</sub>, 3.26% Bi<sub>2</sub>O<sub>3</sub>, 2.99% WO<sub>3</sub>, 2.33% CuS<sub>2</sub>, 0.694% MnO<sub>2</sub>, 0.65% Al<sub>2</sub>O<sub>3</sub> while XRF analysis showed elemental compositions of: 75.194% Bal, 7.168% Sn, 6.146% Zr, 3.471% Fe, 2.976% Nb, 2.027% Ti, 1.176% W, 0.665% Cu, 0.542% Bi, 0.257% Mn and 0.187% Se. The results of HNO<sub>3</sub> acid leaching and tin recovery using neutral extractant showed the highest yield of Sn (94.80%) achieved with 5.0M acid in 360 minutes, 130°C and with the stirring speed of 600 rpm. In overall, the leaching efficiency of Sn (98.70%) and the percentage yield of Sn extracted was found to depend on leaching temperature, time, acid concentration and stirring speed. This could be utilized in scaled-up and optimized production of tin via solvent extraction, for socio-economic development in the era of diversification to the non-oil sector.

Keywords: Mineral, Percentage Yield, Temperature, Acid Concentration.

## Introduction

Globally, the contribution of minerals to the growth of a national economy of a nation cannot be overemphasized and there is no doubt that of all the naturally occurring minerals, metallic mineral ores seem to be more abundant in the Earth-crust compared to other mineral resources such as natural

gas and petroleum [1]. © CSN Zaria Chapter Currently, it is estimated that Africa holds up to 30% of the world's mineral reserves and accounts for more than 20% of the global annual production of five key minerals namely, 80% of global platinum production, 77% of cobalt, 51% manganese, 46% of diamonds, 39% chromium and 22% of gold [2, 3].

In Nigeria, before the discovery of petroleum, tin mining activities particularly in Jos South of Plateau State, Nigeria was one of the sources of revenue to the government. Back then, Nigeria was one of the largest producers of tin and was exporting up to four percent of world tin [4]. At the moment, petroleum and natural gas appear to be the major areas of focus by government for revenue, foreign exchange and international trade with lesser attention to the diversification of economy particularly the development of the solid minerals' sector for mineral ores processing and metal extraction.

In terms of mineral resources, Nigeria is graciously and abundantly blessed with mineral ore deposits but besides ore resource endowments, other critical including utilization of factors modern technologies for mineral ores' processing and extraction of metals to create international trade environment and the impact of solid minerals on Nigeria's economy will continue to depend on the country's ability to successfully leverage its competitive advantage through effective processing of mineral ores into concentrates and extraction of valuable metals [2]. In addition to export earnings, Nigeria in particular and African countries in general have aspired to derive greater economic value from their mineral resources and one of the most assured ways is through mineral ores' processing for extraction of metals [2]. As Indonesia and other countries of the world (Germany, China, Brazil, Bolivia, Namibia,

Portugal, England etc.) are rich nations with abundant natural resources such as metallic minerals' species, one which is cassiterite [5], Nigeria is equally very rich in cassiterite deposits. In fact, cassiterite ores and the tin found in Jos, Plateau State Nigeria is supposedly much stronger and of high quality [6].

Cassiterite is a natural mineral ore that can be extracted economically and it is the principal ore commonly used for extraction of tin metal [5] and with widespread deposits in medium- to hightemperature hydrothermal veins and greisen, in granite, granite pegmatite, rhyolite and in large alluvial placers geological locations [7]. Apart from being the major source of tin metal, cassiterite (SnO<sub>2</sub>) as tin oxide mineral has many other possible merits and one of which is being used in catalyst manufacturing (tin chemical), and for instance in coating of conductive glass FTO (Fluorine Tin Oxide) or as SnO<sub>2</sub> pigments [5, 8].

Additionally, the persistent high demand for tin metal for production of tin cans for food drinks and beverages in industries, alloys, sheet glass, tin foil and particularly soft solder for electronic industries has equally placed high demand for cassiterite ore. Today, owing to recent developments in telecommunication industry especially GSM, cassiterite ore and tin metal constitute vital inputs for a growing range of mass consumer of electronics and some military applications [9]. Figure 1 shows the percentage utilization of tin metal currently in the industrial world [5].

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Figure 1: Chart of Percentage World Utilization of Tin Metal in the Year 2024, [5]

Meanwhile, it been reported that cassiterite in pure state contains up to 78.6% of tin, but pure cassiterite ore is often rarely found [5]. Since cassiterite mineral ore (SnO<sub>2</sub>) is the primary source of tin metal with tin content in most reported ores being varied between 73-75% [5], tin metal is usually economically extracted from purified cassiterite ores. However, tin extraction method depends on the type of ore itself according to the oxidic or sulphide chemical composition [10]. During the past few decades, pyrometallurgical techniques (heating and smelting of cassiterite ore) was extensively used for extraction of tin metal from cassiterite ore, however, it is rapidly being replaced by hydrometallurgy due to its less efficiency and causing environmental problems such as air pollution [11]. According to researchers, when the chemical processing of a metal's ore is conducted in an aqueous environment, the technology

employed is regarded as hydrometallurgy and it involves three distinct stages [12].

Today, owing to recent developments in the field of metallurgy, hydrometallurgy is typically divided into three general areas: oxidative leaching for metals extraction, purification or solution concentration and purification, and the recovery of metal [13].

In the past years, it has been a common yard stick to agree that hydrometallurgy is a technique within the field of extractive metallurgy commonly employed for the extraction of metals from their ores and it involves the use of aqueous solutions for the recovery of metals from ores, concentrates, and recycled or residual materials [13].

Often, hydrometallurgical methods of metal extraction and purification have been accomplished through the use of leaching or solvent extraction or both methodologies which are eco-friendly, efficient and require low-cost operational activities in terms of capital investment and low energy consumption [14].

According to the researcher Habashi [13], leaching involves the use of aqueous solutions either acids or alkalis to extract metal from metal bearing materials when the solution is brought into contact with a material containing a valuable metal. Therefore, chemical leaching method is often primarily used with the aim of extracting metals with very high degree of purity [14] and as eco-friendly chemical process.

In fact, so far only morphological, mineralogical and elemental analysis reports on cassiterite ores from Plateau State, Nigeria are available, and earlier studies elsewhere have shown limited information concerning direct extractions of tin from cassiterite ores using acidic leaching methodology. This study was therefore designed to evaluate the acidic leaching of cassiterite ore mined from Du in Jos South of Plateau State Nigeria, as potential mean for possible development of industrial methodology for commercial extraction of tin by acidic leaching and nitric acid (HNO<sub>3</sub>) leaching was considered in an attempt to enhance the extraction of tin metal from the studied cassiterite ore.

### **Materials and Methods**

#### **Sample Collection**

The cassiterite sample  $(SnO_2)$  used in this study weighing up to 5.0 kg was bought from local miners from different mining sites (i.e. 5 mining sites) scattered within an area in Du community of Jos South Local Government Area of Plateau State, Nigeria. Thereafter, 400.0g of the cassiterite ore obtained from each mining site was measured out and were mixed together and then sun dried before being ground using a mechanical crusher (PEF 125 x 100; 5-25mm, China).

### **Sample Preparation**

The 2.0 kg cassiterite tin ore was crushed into 1inch size using a laboratory jaw crusher (PEF 125 x 100; 5-25mm, China) and then followed by homogenization and sieving using a mesh of woven metal wires that provided a uniform distribution of fixed-size apertures, followed by using ASTM of sizes 5.6mm (Stainless Steel, USA) and then was divided into two equal portions. One portion was further crushed to less than (-2.0 mm) particles using jaw and roller crushers. The samples were then riffled to obtain representative sample by using a Jones Riffler equipment (model, Legend Inc. Sparks USA).

The representative sample was in addition milled into a powder form by using a laboratory ball mill (-0.02 mm) and the well-prepared power form of the sample was used for mineralogical analysis and leaching experiments.

### **XRF and AAS Analysis**

For the XRF analysis, 50.0g portions of fine powder of the ore sample was mixed with a binding aid and then pressed to produce homogeneous sample pellets and thereafter the samples were subjected to XRF analysis using Thermo Fisher Scientific Machine, (2 Radcliff Road, Tewksbury, Ma 01876, USA; XL3-98293). For the Inductively Coupled Plasma– Graphite Furnace Atomizer Absorption Spectroscopic analysis (PerkinElmer, MA, USA), 50.0g of the powdered ore sample was digested to obtain the required sample solution and thereafter, the sample was directly placed in Graphite Furnace atomizer and then electrically heated to a high temperature of 1000°C and in several steps to dry the sample, form ash matter and then vapourised the analyte atoms.

#### **Ore Leaching Analysis**

The analyses were performed in 500 cm<sup>3</sup> glass flask reactor for six hours using three different concentrations (1.5, 3.0 and 5.0 M) of HNO<sub>3</sub>, and at 130°C. For each set of acid leaching analysis, 250 cm<sup>3</sup> of HNO<sub>3</sub> acid was heated on a temperaturecontrolled hot plate equipped with a magnetic stirrer and Digital control system with stirring range of 0-1500 rpm (ISO9001, Jiangsu, China) that maintained temperature with accuracy of  $\pm$  0.99, and was added to 50.0 g of powdered cassiterite ore (-0.02 mm) to maintain the ratio of liquid to solid of 5.0 cm<sup>3</sup>/g. As various concentrations of the HNO<sub>3</sub> acid were added to the ore sample at different temperatures, stirring speed of 600 r/min was maintained with Teflon-coated stirring bar and the time of digestion of the sample at each specific temperature was determined.

Also, the leached solution pH was kept at approximately 4.15 by addition of 1.0 M solution of oxalic acid. The leaching pH maintained in this work was considered to enhance the effectiveness of dissolution of the ore, leaching efficiency of the process and the solubility of tin metal in the lixiviant solution [15, 16]. After leaching for a period of time and no further reaction was observed, the time for each leaching experiment (60, 120, 180, 240, 300 and 360 minutes) was taken using a stop watch and the suspensions (leached liquors) were filtered, and the residue was washed with deionized water severally and dried for analysis. For each set of conditions, tests were performed in triplicates, and the average leaching efficiencies were reported in this work.

The effects of temperature  $(30, 50, 70, 90, 110, 130 \circ C)$  and nitric acid concentration (1.5, 3.0, and 5.0) on Sn metal yields were assessed [15, 16, 17]. At this point, it should however be mentioned that the acid concentration and leaching time were considered as independent variables in the leaching investigation.

## Determination of Leaching Efficiency and Tin Metal Recovery Analysis

The leaching efficiency was evaluated using the following relationship as reported in Banihashemi *et al.* [18].

$$LE (\%) = \frac{(Msn X CMsn - MRLsn X CLR)}{(Msn x CMsn)} X$$

100; where LE (%) is the leaching yield of Sn,  $M_{Sn}$  is the mass (gr) of the molten sample,  $CM_{Sn}$  is the content (%) of Sn in the molten sample,  $MRL_{Sn}$  is the mass (gr) of the leaching residue and  $C_{LR}$  is the content (%) of Sn in the leaching residue.

After leaching reaction, the recovery of tin metal from the pregnant leach solution was basically carried out as reported by Lee *et al* [19] using tributyl phosphate (TBP) as an extractant for recovery of tin metal from the leached solution. The percentage of tin metal recovered or extracted from the leached solution was determined according to the methodology and the relationship reported in Zheng *et al* [20], and the relationships between percentage yield of Sn metal extracted and leaching time and temperature respectively were extrapolated.

## **Results and Discussion**

Mineral	Percentage Composition (%)	Composition in PPM	
SnO <sub>2</sub>	60.98	609800	
SiO <sub>2</sub>	8.70	87000	
$ZrO_2$	5.70	57000	
$Fe_2O_3$	5.56	55600	
NbO	4.81	48110	
TiO <sub>2</sub>	4.07	40675	
Bi <sub>2</sub> O <sub>3</sub>	3.26	32628.2	
WO <sub>3</sub>	2.99	2986	
$CuS_2$	2.33	23250	
MnO <sub>2</sub>	0.694	6939	
$Al_2O_3$	0.65	6500	
K <sub>2</sub> O	0.0603	602.50	
$As_2O_3$	0.063	629	
$SeO_2$	0.065	649	
Na <sub>2</sub> O	0.0449	449.29	
LOI	0.22	2200	

### **Mineralogical Characterization**

The results of significant mineralogical composition of the ore (Table 1) have revealed that the sample is composed mainly of 60.98% of tin oxide (SnO<sub>2</sub>), 8.70 % of quartz (SiO<sub>2</sub>), 5.70 % of baddeleyite (ZrO<sub>2</sub>), 5.56% of haematite (Fe<sub>2</sub>O<sub>3</sub>), 4.81% of greyish oxoniobium or niobium (II) oxide (NbO) and 4.07% of titania or anatase (TiO<sub>2</sub>). Other significant minerals in the ore include 3.26% of

bismite (bismuthinite) or bismuth trioxide (Bi<sub>2</sub>O<sub>3</sub>), 2.99% of tungsten trioxide or tungstite (WO<sub>3</sub>), 2.33% of villamaninite (CuS<sub>2</sub>), 0.694% of pyrolusite (MnO<sub>2</sub>) and 0.65% of bauxite (Al<sub>2</sub>O<sub>3</sub>). Basically, the convincing interpretation of the results is that the cassiterite ore is composed of two significant minerals which are mainly oxides and sulphide minerals. Other minerals also identified as minor segments of interest were Na<sub>2</sub>O, K<sub>2</sub>O, As<sub>2</sub>O<sub>3</sub>,  $SeO_2$  etc. It is pertinent to note that the ore densely rich in tin oxide which was identified to be the most important and significant mineral and the ore is also moderately rich in haematite mineral for extraction of iron metal.

Meanwhile, comparatively, the report of mineralogical characterization of Kuru cassiterite ore in Plateau State, Nigeria by SEM-EDS, XRD and ICP techniques by Ogwuegbu et al [4] claimed that the cassiterite ore examined contained 13.18%

of cassiterite, 4.05% of rutile, 3.55% of coffin, 2.06% of Siderophylite, 3.28% of Tilleyite, 1.05% of Zircon, 1.94% of Manganocolumbite, 9.98% of Quartz and 1.01% of Monazite. Elsewhere, Firdiyono and co-workers [21] highlighted that the investigated tin ore contained the main minerals of cassiterite (SnO<sub>2</sub>) and associated minerals such as columbit-tantalite [(Fe, Mn) (Ta, Nb)<sub>2</sub>O<sub>6</sub>], zircon (ZrSiO<sub>4</sub>), ilmenite (FeTiO<sub>3</sub>), rutile (TiO<sub>2</sub>), quartz (SiO<sub>2</sub>), pyrite (FeS<sub>2</sub>), xenotime (YPO<sub>4</sub>) and monazite (Ce, La, Y, Th) PO<sub>4</sub>.

Table 2: Result of Significant Elemental Compositions of the Cassiterite Ore

Element	Percentage Composition (%)	± Error
Bal	75.194	±0.403
Sn	7.168	±0.150
Zr	6.146	±0.105
Fe	3.471	$\pm 0.047$
Nb	2.976	±0.052
Ti	2.027	±0.027
W	1.176	$\pm 0.069$
Cu	0.665	±0.011
Bi	0.542	±0.010
Mn	0.257	±0.012
Se	0.187	$\pm 0.018$

#### **Elemental Characterization**

The XRF result shows the elemental compositions in the cassiterite ore (Table 2) with boron aluminide (Bal) being identified as the most abundance component (75.194 %) of the ore. Tin metal (Sn) in the ore which is present both as free metal (7.168 %) and in the oxide form (SnO<sub>2</sub>) was the second most significant component of the ore. Other metals in the ore found with significant values include, Zr (6.146%), Fe (3.471%), Nb (2.976%), Ti (2.027%) and W (1.176%). One fascinating discovery about the cassiterite ore is the identification of Bal that has no known record of occurrence in association with mineral ores. Boron aluminide (Bal) is a highly valued alloy with high demand in aerospace industry and the identification of the alloy in association with the cassiterite ore has placed a high value for the ore. However, more work and further analysis are required for the recovery of the Bal from the cassiterite ore as its recovery would be of great value to both the state and the national economy. Meanwhile, there are some indications of slight differences in the results of the elemental characterization of the analysed cassiterite ore with the results of elemental analysis by ICP-OES reported in [4] with elemental values of: Sn (28.0%), Si (5.5%), Fe (5.16%), Nb (2.53%), Ti (3.51%), Al (2.48%), Y (1.6%), La (1.13%), P (0.88%), Zr (0.99%) and Mn (0.31%) while other trace elements found in their trace quantities

according to the report include; U, Ce, K, Na, Mg and Ca.

In addition, it was also found that another cassiterite in Indonesia contained, Sn (57.87%), La (3.43%), Ce (3.37%), Nd (2.18%), Fe (1.79%) and Ti (1.45%) while other trace elements found include, Ca, Mg, Al, Si, Zr, W and Pb [5]. Nevertheless, in many clarifications, it has been argued that differences in mineralogical and elemental compositions of ores may be attributed to a number of factors including the type of rocks and minerals availability in the soil and the geological disposition of an ore deposit.

#### Effect of Acid Concentration, Temperature and Sn Metal Extraction Yield

Time (Mins)	Temp. (T in °C)	Acid Conc. (M)	% yield of Sn
60	30	1.5	16.40
120	50	1.5	30.90
180	70	1.5	43.40
240	90	1.5	53.90
300	110	1.5	62.50
360	130	1.5	69.00

Table 3: Effect of HNO<sub>3</sub> Acid Concentration (1.5) and Temperature on Extraction Yield of Tin Metal with Time

The results of acid leaching of the cassiterite ore (Table 3) show that the percentage yield of tin metal increases with increase in temperature and with time (Figure 2.0). At 60 minutes, and 30 °C, only 16.40% yield of Sn was recorded but as time was increased to 360 minutes and temperature 130 °C, the yield was 69.0%, using acid concentration of 1.5

M (Figures 2.0 and 3.0). Meanwhile, when the acid concentration was increased to 3.0 M, the percentage yield of Sn was increased from 24.58% at 60 minutes and at 30 °C to 77.20% at 130 °C and 360 minutes (Table 4) and the relationship between the acid concentration, leaching time and temperature with the percentage yield of tin metal

is shown in Figure 4.0. In accordance with the leaching requirement, the leaching liquor was vigorously stirred at 600 rpm for six hours (360 mins) and typically, the powdered form of the cassiterite ore used in addition greatly facilitated the rapid leaching process from 1.0 hour to 6.0 hours and under the condition of atmospheric pressure.

More interestingly, when the acid concentration was increased to 5.0 M, the Sn metal yield increased from 24.58% to 41.70% at 60 minutes and 30 °C (Table 5). Furthermore, when the temperature was increased to 130 °C and in 360 minutes, the yield of Sn was observed to increase from 77.20% to

94.80% (Table 4 and 5). From the observations drawn from the results of the acid leaching, it is important to note that Sn metal yield generally increased with increase in concentration of the acid leachate, leaching temperature and time. Additionally, smooth leading curves for percentage of Sn metal yield versus leaching temperature were obtained (Figures 3.0, 5.0 and 7.0) for each acid concentration. The curves indicated that with each concentration of the acid leachate, the lowest percentage yield of Sn metal was obtained at 30 °C, 16.4% with 1.5 M acid, 24.58% with 3.0 M acid and 41.70% with 5.0 M acid in 60 minutes of each leaching reaction.



Figure 2.0: Effects of Acid Concentration (1.5 M), Leaching Time and Temperature on Percentage Vield of Sn Metal.

ChemClass Journal Vol. 9 Issue 1 (2025); 425-441 Effect of Temperature on % yield of Sn 69 80 62.5 Percentage (%) Yield of Sn 53.9 60 43.4 30.9 40 16.4 20 0 20 40 60 80 100 120 140 0 Leaching Temperature in oC

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---- % yield of Sn

However, the highest percentage yield of tin metal (94.80%) was recorded at the temperature of 130 °C and with acid concentration of 5.0 M in 360 minutes. At the same temperature of 130 °C but with lower acid leachate concentration of 1.5 M and 3.0 M, only 69.0% and 77.20% of tin metal respectively were obtained from the cassiterite ore with 5:1 (5.0 cm<sup>3</sup>/g) acid-ore ratio (i.e.  $250 \text{ cm}^3$  acid leachate: 50 g of powder cassiterite ore).

Table 4: Effect of HNO<sub>3</sub> Acid Concentration (3.0 M) and Temperature on Extraction Yield of Tin **Metal with Time** 

Time (Mins)	Temp. (T) in °C	Acid Conc. in (M)	% yield of Sn
60	30	3.0	24.58
120	50	3.0	39.09
180	70	3.0	51.59
240	90	3.0	62.10
300	110	3.0	70.60
360	130	3.0	77.20

Based on the foregoing and the results shown (Table 3, 4 and 5), it appears appropriate to infer that the percentage yield of Sn metal is a function of concentration of the lixiviant solution and temperature. Also, it was desirable to use the stirring speed of 600rpm instead of using 120 or 300 rpm to observe the effect of stirring speed on the leaching efficiency of ore.



Figure 4: Effects of Acid Concentration (3.0), Leaching Time and Temperature on Percentage Yield of Sn Metal



Figure 5.0: A Graph of Effect of Temperature on Percentage Yield of Sn Metal With 3.0 M Acid Concentration

As a result, it was also found that the leaching efficiency was increased with the use of 600 rpm stirring speed and this is especially true as only 71.10% of Sn was determined when the stirring speed of 300 rpm was maintained with 50 g of cassiterite ore in 250 cm<sup>3</sup> of 5.0 M of the leachate

acid and at 90 oC and 240 minutes. However, with the stirring speed of 600 rpm at 130 °C and in 360 minutes, leching efficiency of 98.70% was achieved. Again, it should be understood that to facilitate the leaching reaction, the stirring speed was increased to enhance a higher leaching efficiency. It is equally worthwhile to become aware that the pH of a leaching reaction often plays crucial role in influencing leaching effectiveness, efficiency and metal extraction yield in mineral ores' leaching processes [16, 17].

Frequently, optimal pH conditions are usually occurred at either acidic or alkaline pH depending

largely on the specific metal and the leaching method employed [16, 17]. Essentially, many research reports have underscored that pH plays an important role in ore leaching processes [15, 17]. This is especially true as Apua and Madiba [16] reported the recoveries of 81.25% of copper, 90.01% of cobalt and 79.68% of iron when the leaching pH reached 1.0 and the pH used for the leaching analysis at the range of 0.5 to 4.0 enhanced the maximum extraction of the metals with H<sub>2</sub>SO<sub>4</sub> acid as the pH reached 1.0. However, the authors conclusively asserted that from pH of 1.0, the dissolution of Cu, Co and Fe declined as the pH value was increased [16].

Table 5: Effect of HNO3 Acid Concentration (5.0 M), Leach	ing Time and Temperature on Extraction
Yield of Tin Metal with Time	

Time (Mins)	Temp. (T) in °C	Acid Conc. in (M)	% yield of Sn
60	30	5.0	41.70
120	50	5.0	56.20
180	70	5.0	68.70
240	90	5.0	79.70
300	110	5.0	88.30
360	130	5.0	94.80

The Sn metal yields as a function of time at different temperature was studied and the results were plotted in Figure 2.0. The percentage yields of Sn metal were increased sharply with every twentydegree rise in temperature and increased gradually with twenty minutes prolonging of time.

The data (Table 3, 4 and 5) suggest relatively fast leaching process during the time interval of twenty minutes followed by steady increased yield of Sn metal from low concentration of the acid to a higher acid concentration. These observations are quite different from that of leaching of rare earth elements such as lanthanum, praseodymium, and neodymium in sulphuric acid from rare earth element slag reported by [22,15].

Notably also, as the temperature was increased, the leaching efficiencies of the tin metal was promoted gradually with increasing time. However, the

marked advantage of the acid leaching was the low temperature utilized which showed significantly better results with less volume of acidic waste to avoid the discharge of such liquid wastes into water or on land.



Figure 6.0: Effects of Leaching Temperature, Time and Acid Concentration (5.0 M) on Percentage (%) Yield of Sn



Figure 7.0: Effect of Temperature on Percentage Yield of Sn Metal With 5.0 M Acid Concentration

The percentage Sn metal yields from the cassiterite ore as a function of time at different temperature

and acid concentration was studied and the results were plotted as in Figure 2.0, 4.0 and 6.0 for each

acid concentration. The metal yields were increased sharply for each twenty minutes and increased gradually with the prolonging of time. Again, the data in Table (3, 4 and 5) suggest a relatively fast leaching process during each twenty minutes time interval followed by a constant increase in the percentage yield of tin metal. As the rise of temperature occurred by 20 °C in each case of different acid concentration, the leaching efficiencies of the cassiterite ore were also promoted gradually with evidential increased in the percentage yield of Sn metal. However, it was only increased when the temperature was increased steadily and considering the energy cost, 130 °C was utilized in the leaching experiments.

On the other hand, this research team argues that the leaching rates of the cassiterite ore can be increased by optimization of certain factor such as the leaching time and also the stirring speed and acid concentration. These observations indicate that optimization of the factors can show significantly better results for tin metal yield particularly with regard to the speed with which (98.70%) dissolution or leaching of the ore was achieved. As might be expected, one other important factor affecting the Sn metal yield was temperature and up to 98.70% of Sn was noted to readily dissolve at high temperature than at lower temperature.

Meanwhile, it is also necessary to argue that although cassiterite ore does not dissolve in pure cold acid like sulphuric and nitric acid solutions, however, the reaction of tin metal with HNO<sub>3</sub> often depends on the concentration of the acid and the acid temperature and some dissolution of tin metal in the leaching systems can be attributed to the amphoteric nature of tin metal with the formation of tin trioxonitrate (V) salt during the oxidation leaching process as shown in the proposed leaching equations 1.0, 2.0, 3.0 and 4.0.

$$Sn_{(s)} + 2HNO_{3(aq)} \longrightarrow Sn(NO_{3})_{2(aq)} + H_{2(1)} \dots Equ. (1.0)$$

$$Sn_{(s)} + 4HNO_{3(aq)} \longrightarrow Sn(NO_{3})_{4(aq)} + 2H_{2(1)} \dots Equ. (2.0)$$

$$Sn^{2+}_{(aq)} + 2HNO_{3(aq)} \longrightarrow Sn(NO_{3})_{2(aq)} + 2H^{+}_{(aq)} \dots Equ. (3.0)$$

$$Sn^{4+}_{(aq)} + 4HNO_{3(aq)} \longrightarrow Sn(NO_{3})_{4(aq)} + 4H^{+}_{(aq)} \dots Equ. (4.0)$$

$$Sn_{(s)} + 2H_{2}SO_{4(aq)} \rightarrow SnSO_{4(aq)} + SO_{2(g)} + 2H_{2}O_{(1)} \dots Equ. (5.0)$$

In addition, the  $HNO_3$  acid was particularly preferred to  $H_2SO_4$  in this investigation because the Sn metal closely associated with encapsulated other mineral compounds in the ore was selectively dissolved in the acid during the leaching process. Furthermore, the release of SO<sub>2</sub> gas when  $H_2SO_4$  is

used for the leaching of cassiterite (Equ. 5.0), also discouraged the use of the acid.

### Conclusion

This study demonstrates the beneficial effect of chemical leaching of cassiterite ore via nitric acid treatment for the extraction of tin metal by

application of neutral extractant. Nitric acid leaching of cassiterite ore has appeared to significantly improve the extraction of tin metal from the ore. Based on the above studies carried out for the leaching of tin metal from powdered cassiterite ore under varying acid concentration, temperature and time, the following conclusions are drawn: (i) Nitric acid is an effective leachant for tin metal which selectively dissolves tin from the cassiterite ore containing other metals such as iron, titanium, manganese and others. (ii) A leach recovery of 94.80% of tin was obtained from the cassiterite ore with 5.0 M of HNO<sub>3</sub>. The dissolution of tin from the powdered tin ore was found to be 95.60% using 5.0 M HNO<sub>3</sub> at 110°C in 300 minutes at fixed S:L ratio 1:5, and further percentage dissolution was found to increase up to 98.70% with increase in temperature to 130 °C and leaching time of 360 mins and the percentage Sn metal yield of 94.80% was recovered. Probably, the existence of other reactive substances in the leaching liquor, can be blamed for these differences between the dissolution value and the total percentage yield value of Sn metal recovered.

In general, these findings show that the chemical leaching method such as nitric acid treatment of cassiterite ore can be suitably used for dissolution of tin metal from the ore before precipitation or solvent extraction or electrowinning even in industrial scale for high yield of Sn metal. Therefore, hydrometallurgical methods of cassiterite ore leaching and Sn metal recovery are relatively cheap and fast processes. On a final note, an emerging perspective which is being recommended is that of a global view for sustainable extraction of metals from natural mineral resources like cassiterite ore which is to reduce environmental pollution by using ecofriendly, green chemistry technologies like acid leaching hydrometallurgical process as being considered a better option in this work.

### **Declaration of Competing Interest**

The authors of this work declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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