AN OVERVIEW OF SUSTAINABLE COPPER RECOVERY METHOD VIA BIOLEACHING

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Abstract- Since early 1930s, the copper mining industry has been the economic and social pillar of Zambia with about 80% contribution to the total export earnings and about 13% Gross Domestic Product (GDP). However, the copper mining industry has been employing traditional techniques which have disruptive effects such as land degradation, air and water pollution which pose long term threats on the local livelihood of the people and biodiversity. Furthermore, the ore mineralogical composition has changed through the years of exploitation of the copper in Zambia, the copper oxides have become scarce; the only sources of copper are sulfides, and its content has diminished down to approximately 1%. Bioleaching has emerged as an alternative and sustainable technology with great potentials to process bulky low grade sulphide mineral ores with minimum environmental degradation using low capital expenditure. This study looks at an overview of copper mining in Zambia and presents new opportunities related to the development of sustainable method for copper recovery by means of bioleaching. The Zambian Copperbelt is part of the Central African Copperbelt which forms one of the world's largest metallogenic provinces containing one-fifth of all global copper resources with low grade. Reports show that more than one billion tons of ore (c.2.7% Cu) has so far been mined from the mines on the Copperbelt Province of Zambia and conservative estimates suggest that a further two billion tons await exploitation. This provides considerable opportunities for further exploration and mining in the country. Zambia needs to focus its effort on research in bioleaching process and its application to achieve sustainable copper recovery within the context of economical, ecological and social sustainability.

Index Terms- Bioleaching, Copper Extraction, Sustainable Mining, Mining in Zambia.

I. INTRODUCTION

Global copper mine production has historically been geographically concentrated in South America, with Chile and Peru accounting for around 40 per cent of annual global production [1]. Analysts maintain that, at current production rates, traditional supply regions will be unable to meet expected global requirements by 2020 [2]. As such, new sources of supply will need to be identified and projects in the pipeline fast-tracked. In this regard, Zambia has the potential to contribute significantly to meeting global requirements for refined copper in the long-term due to the presence of the Central African Copperbelt. The Copperbelt region contains one-fifth of all global copper resources with grades of about 1 - 2 per cent and in some instances, 7 - 8 per cent copper [3]. This region occupies a major geological structure called the Lufilian Arc that extends over a distance of more than 500 kilometres from Kolwezi in the southern parts of the Katanga Province, DRC, to Luanshya in Zambia [4]-[5]. Furthermore, huge low grade copper deposits (~0.67% Cu) were discovered in North-western Zambia [4]. The study carried out by [6] projected that even over 100 years of production there will still remain huge resources of copper and cobalt deposit in addition to sources in the form of old plant tailings in the region. Metallurgical extraction processes have been employing traditional techniques (pyro-metallurgy and hydro-metallurgy) which involve crushing and grinding of copper-containing ore, followed by application of tremendous amount of heat or toxic chemicals. These methods are relatively inefficient, and as much as 1-2 per cent copper is lost in such tailings. The study conducted by [7] revealed that tailings dams operation is one of the most important anthropogenic sources of disruptive effects such as land degradation, water, air pollution as well as geotechnical issues which pose long term threats on the local livelihood of the people and the environment and biodiversity. Acid mine drainage (AMD) has been reported on two hectares of an old ore stockpile in Chibuluma mining area in Kalulushi district [8]. The report further states that drainage water from this area which has contaminated a nearby watercourse holds a pH of 2.0 – 3.0 and elevated concentration of copper and cobalt. Soils in large areas within the Copperbelt province are known to be contaminated by a variety of elements in addition to copper and cobalt. The highest concentrations for heavy metal contamination of the soils are geographically directly associated with the districts of Kitwe, Mufulira and Chingola, and also to a lesser extent with Kalulushi, Chililabombwe and Chambishi [8].

Future sustainable development in mineral processing requires evaluation of the environmental impact of the mining activities before, during and after operation. This entails application of novel technologies that can result in metal recovery from sources that have not been of economical interest [9]. Retreatment of tailings wastes in addition to low grades deposits that have not yet been explored could be considered to be high potential source of copper which can contribute to creation of an opportunity for expansion and

development of new operations in Zambia over the longer-term [10]-[11].

Metal recovery by biological process 'bioleaching' has emerged as an alternative technology today especially in metals like copper and gold [12]. Bioleaching involves the natural ability of some microorganisms to solubilise some mineral constituents of rock or ore [13]. Most commonly used bioleaching microorganisms are chemolithoautotrophic and thus use inorganic energy and carbon sources. They use ferrous iron and/or reduced sulfur compounds as an energy source, and chemical elements commonly found in ores, particularly in copper ores. This technique of metal extraction is reported to deliver significant environmental benefits because it uses less energy and does not produce dust and SO_2 emissions when compared to traditional treatment methods [14]. Under bioleaching process, Sulfur is converted to soluble sulphate and is retained in the aqueous phase. Other benefits associated to the process include; low capital and operating cost, the use of naturally occurring key components (microorganisms, water and air) and the use of atmospheric pressure and ambient temperature conditions [15]. The commercial application of bioleaching process relies on the knowledge of the mechanisms and the extent of adsorption of chemical elements or compounds by microorganisms. The future development of copper extraction in Zambia with regards to environmental concerns, waste tailings and low-grade copper ores treatment has motivated this research. The aim of this study is to provide an overview of copper mining in Zambia and presents new opportunities related to the development of sustainable method for copper recovery by means of bioleaching.

II. GEOLOGY AND MINERALISATION OF THE ZAMBIAN COPPERBELT

The Zambian Copperbelt is part of the Central African Copperbelt which forms one of the world's largest metallogenic provinces containing one-fifth of all global copper resources [3]. The Copperbelt occupies a major geological structure called the Lufilian Arc that extends over a distance of more than 500 km from Kolwezi in the southern parts of the Katanga Province, DRC, to Luanshya in Zambia. This region is characterized by the rocks of the Katanga system, which were formed during the Neoproterozoic Age [16]. The geology comprises argillaceous and carbonate shale, limestone and dolomite of the Upper Roan, Mwashia, Kakontwe and Kundelungu formations [4]. The study carried out by [17] showed that the type of ores in the Copperbelt region are stratiform to stratabound, characterized by finely disseminated copper – cobalt – iron sulfides (predominantly chalcopyrite, $CuFeS_2$, cobaltiferous pyrite, $Fe(Co)S_2$, and bornite, Cu_5FeS_4, in host rocks that may include quartzite (arkose), shale and dolomite. The study further indicated that huge low grade copper deposits (~0.67% Cu) which are dominantly sulphides (chalcopyrite) were discovered in Lumwana area in the North-western Zambia.

III. HISTORICAL BACKGROUND OF BIOLEACHING

Bioleaching of mineral ores for metal recovery has been practiced for centuries. There is evidence found at Rio Tinto, Spain, in the 18th century that ancient people where recovering leached copper from acidic waters [19]. These mines have been exploited since pre-Roman times for their copper, gold, and silver values [20]. However, the development of this biotechnology actually started in circa 1950, once bacteria involved in the leaching of copper were isolated and characterized [21]. An early documented commercial application of a bioleaching process in the mining industry was for copper extraction from mine waste [22]. Reference [23] reported the role of the iron oxidizing Acidithiobacillus ferrooxidans in leaching of uranium. The uranium ore was stacked in heaps, similar to dump leaching of low-grade copper ore, and leached using an acidic ferric sulfate solution at the Elliot Lake Mine, Ontario, Canada. Reference [24] reported that commercial application of bioleaching at the Lo Aguirre mine in Chile where about 16,000 tons ore/day of copper was processed between 1980 and 1996 using bioleaching from heaps. Since 1980, research and development activities in bioleaching have flourished rapidly and numerous copper heap bioleach operations have been commissioned [11]. In the same 1980s, a first bioleaching plant in Africa was commissioned at the Fairview Gold Mine near Barberton in South Africa. The technology of bioleaching has recently become a competitive and preferred process to conventional ones.

IV. DESCRIPTION OF BIOLEACHING

Bioleaching is the extraction of metals from ores using the principal components of water, air and microorganisms [25], all of which are found readily within the environment. In the case of copper extraction, copper is liberated from its copper sulphide bearing ores such as chalcopyrite, covellite, chalcocite using micro-organisms [26]-[27]. According to [28], the microorganisms responsible for bioleaching derive energy from the oxidation of ferrous ions, the oxidation of sulphur and the fixation of carbon dioxide. There are various types of techniques that exist within the bioleaching. Currently, the two prominent methods are Tank and Heap bioleaching. Tank bioleaching involves large aerated tanks to facilitate continuous flow mode of operation [26]. Heap bioleaching involves stacking crushed ore on

plastic mats and spraying a solution with liquor solution containing microorganisms with rich microbial nutrients The process of bioleaching for the extraction of copper have been used for the commercial production of copper. Reference [24] reported that one of the biggest dump leaching sites at the Kennecott Bingham Canyon Mine in Utah, USA has produced as much as 200 tons of copper per day which accounts for approximately 25 percent of the world's copper production. In recent years, the use of bioleaching of copper in the industry has come of age. The most significant current application of microorganisms in this field is heap bioleaching as well as aerated stirred tank reactors. In 2002, Mintek, BacTech and Peñoles joined forces in a venture to commercialise base-metal bioleaching technology at Monterrey, Mexico, with the emphasis on treating mixed sulphide and chalcopyrite–bearing concentrates. Currently, the plant is processing about 0.5 tons/day of copper concentrates in order to demonstrate the viability of the bioleaching process [29]. However, there is a lack of specific details in the literature about organisms and conditions used in industrial applications.

V. MICROORGANISMS IN BIOLEACHING

A variety of microorganisms is found in leaching environments and has been isolated from leachates and acidic mine drainage [30]. Reference [31] observed that these systems can show high levels of microbial biodiversity including chemolithotrophic bacteria, for example Thiobacillus ferrooxidans (T. ferrooxidans) and closely related species, the second are heterotrophic microbes, including bacteria, fungi and yeast, such as Bacillus mucilaginosus, Aspergillus niger and related species. The chemolithotrophic bacteria that are mainly used in bioleaching are acidophiles, growing at pH values in the range 1.5 – 4.0 and autotrophs, getting their energy from the oxidative attack of the metal sulphides that they solubilise. The chemolithotrophic bacteria get their carbon for assimilation from CO_2 and their nitrogen from inorganic compounds [32]. In contrast, the heterotrophic microbes use organic compounds as their energy and carbon source. They also require appropriate growth conditions such as pH, and a nitrogen source [33]. Reference [32] reported three main groups of the chemolithotrophic bacteria which include the mesophiles, moderate thermophiles and extreme thermophiles. The mesophiles operate between 30 and 42°C; include several species of Acidithiobacillus and Leptospirillum. Moderate thermophiles exist within temperature range of 45 to 55°C, such as Sulfobacillus and Ferroplasma species. The extreme thermophiles thrive between 60 and 90°C and are mostly archaea which include various species of Sulfolobus and Metallosphaera [33].

VI. THE GENERAL MECHANISMS OF BIOLEACHING

The mechanism of bioleaching is complex and still under discussion. A number of hypotheses have been put forward to explain how bacteria can dissolve metal from either metal sulphides or metal oxides. The equations shown below depict the dissolution of desired metal in a bioleaching reaction according to [11]-[34]. The first chemical equation involves ferric-iron (Fe^{3+}) leach reactions with sulphide mineral. The reaction result in a formation of elemental sulphur and ferrous iron and the desired metal dissolved in the liquor. This is followed by re-oxidation of ferrous-iron back to ferric-iron and finally conversion of elemental sulphur to sulphate ions a source of sulphuric acid as shown in equation "(3)," below, through by sulphur oxidising bacteria.

$$MeS + 2Fe^{3+} \rightarrow 2Fe^{2+} + S^{0} \ldots\ldots\ldots Eq.1$$

$$2Fe^{2+} + O_2 + 4H \rightarrow 2Fe^{3+} + 2H_2O \ldots\ldots Eq.2$$

$$2S^{0} + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^{+} \ldots\ldots Eq.3$$

Reference [35] proposed another bioleaching model which considered the bio-oxidation of pyrite using T. ferrooxidans. The hypotheses were: (i) Cell reproduction will occur, extracellular polysaccharides are produced, and iron oxyhydroxides are formed when the cells attach themselves to the oxide/sulphide (ii) iron species act as a mediator, the iron is oxidised at the level of cell attachment and reduced at the oxide/sulphide interface, (iii) sulphur species produced by the action of the mediator at the oxide/sulphide interface diffuses through the surface layers and is either metabolized or passes into the bulk solution. The figure below shows a chematic view of the proposed model.

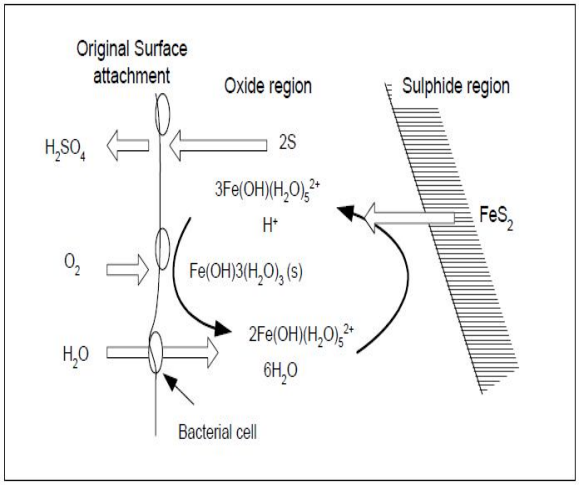

Figure 2.6 Schematic diagram of bioleaching model [34]

The proposed stoichiometry are as follows:
At the oxide/sulphide interface:

$$2FeS_2 + 2H_2O \rightarrow 2Fe(OH)^+S_4^= + 2H^+ + 3e^- \ldots\ldots Eq.4$$

At the bio-film:

$$S_4^= + 16H_2O \rightarrow 4SO_4^{2-} + 32H^+ + 25e^- \ldots\ldots\ldots Eq.5$$

$$2Fe(OH)^+ + 4H_2O \rightarrow 2Fe(OH)_3(s) + 4H^+ + 2e^- \ldots Eq.6$$

Reductive reaction in the bio-film:

$$7.5O_2 + 30H^+ + 30e^- \rightarrow 15H_2O \ldots\ldots\ldots\ldots\ldots Eq.7$$

The mediator reaction:

$$Fe^{2+} \leftrightarrow Fe^{3+} + e^- \ldots\ldots\ldots\ldots\ldots Eq.8$$

Overall stoichiometry:

$$2FeS_2 + 7H_2O + 7.5O_2 \rightarrow 2Fe(OH)_3(s) + 4SO_4^{2-} - 8H^+ \ldots Eq.9$$

VII. FACTORS AFFECTING BIOLEACHING

The rate and efficiency of bioleaching process depends on a number of different factors. These factors include; Physico-chemical and microbiological factors of the leaching environment, roperties of the mineral ores, process parameters such as pH and temperature among others [36].

Reference [37] revealed that metal dissolution by bacterial methods depends upon the nature of the mineral ores, i.e. its chemical composition, its origin. In this study, the effects of ferrous sulphate and ferric sulphate additions on copper extraction were compared for four chalcopyrite samples and the results showed that different sources of chalcopyrite samples have different leaching efficiency. Reference [38] also studied the bioleaching of complex sulphide ores, containing chalcopyrite, sphalerite, pentlandite, pyrite and pyrrhotite, using uncharacterised strains from mines. The results were obscured on various levels. Not only did the relationships between leaching rates and pH, redox potential and ferric ions in solution vary for each mineral, these relationships are not understood for individual ores let alone the complex ones. Recently, there is a lot of research going on to understand bioleaching of complex ores which contain several different minerals.

It has been reported that microbial growth medium plays a critical role in bioleaching. The fundamental elements found in the growth media for example organic carbon may have some benefit for the bacteria by diminishing the toxicity if there is any toxic metal in the solution [39]. Hydrogen is required as a reductant for NAD(P)+ in biosynthetic pathways while ammonia appears to be the nitrogen source and phosphate or sulphate is desired in metabolic balance and growth restriction. Magnesium is used for energy-transducing enzyme activities [31]. In order to improve growth media for bioleaching proposes, different modified media for autotrophic microorganisms have been developed and studied by different researchers [40].

The optimum temperature and pH have been reported to affect growth conditions of microorganisms. These optimum temperature and pH for oxidation and cell growth can vary between strains and is also dependent on experimental conditions. Reference [41] studied temperature effects on bacterial leaching of sulphide ores using uncharacterised strains from mines. The study indicated that at low temperature the rates were slow but as the temperature increased so did the rated. The initially slow rates range was attributed to the lag phases preceding active bacterial leaching. Increasing temperature in the range of 20 - 35°C was found to enhance the biological oxidation rate of ferrous ions by T. ferrooxidans. Reference [42] also reported that the pH in a range of 1.5-3.0 found that the highest biooxidation rate of iron and arsenic using T. ferrooxidans.

The study conducted by [43] proposed that the leaching rates for metal sulphide ores is enhanced with a reduction in particle size. The study compared a range of sizes between +38, -53 µm and +106, -150 µm using of copper and iron dissolution from these ranges of chalcopyrite particles by T. ferrooxidans grown on sulphur, liquid thiosulphate and ferrous ions solution in shake flask cultures. The result showed that leaching rates were significantly higher for the smaller particle range due to the larger surface area available for bacterial attachment.

Other factors reported to have effect on bioleaching process are pulp density and carbon dioxide. Reference [44] studied the optimal pulp density for bioleaching complex sulphide ores using mixed characterised mesophiles from mines. It was observed that there is a significant decrease in metal dissolution when the pulp density was increased from 5 % to 20 % (w/v). The rate and amount of mineral sulphide oxidation is also affected by lack of carbon dioxide as it restricts the bacteria growth. Aqueous-phase carbon dioxide at concentrations of more than 10 mg/l was found to inhibit growth of T. ferrooxidans on pyrite-arsenopyrite-pyrrothite ore [45].

VIII. FUTURE PROSPECTS OF BIOLEACHING IN ZAMBIA

According to [46], more than one billion tons of ore (c.2.7% Cu) has so far been mined from the mines on the Copperbelt Province of Zambia and conservative estimates suggest that a further two billion tons await exploitation. Due to the long term history of mining on the Zambian Copperbelt, the potential exists for the major additional source of copper in the form of old tailings plants. Reference [3] also reported that about 1 – 2% of copper has been lost from the tailings dams due to the relatively inefficiency of metallurgical

extraction processes. Re-treatment of old tailings and low grades deposits that have not yet been explored are high potential sources of copper recovery for current and future investments. The future of sustainable copper recovery, on a large scale, in Zambia depends on intensified research on the amenability of copper sulphide minerals, from various mines in Zambia to bioleaching. Currently, research works focusing on process efficiency to enhance optimal operating conditions that will speed up the microbial oxidation kinetics are now being conducted widely by different organizations. These operating conditions range from simple ones which include sufficient oxygen and carbon dioxide as well as microbial substrates such as ammonium sulphate, potassium sulphate, optimum temperature and pH and any others factors. Research is also conducted on microbial bioengineering on areas of microbial characterization and cloning of bacteria used in bioleaching with emphasis on enhancing environmentally sustainable process. In developed countries, bioleaching technology has reached advanced stages with heap bioleaching being preferred for low-grade copper tailings and ores whilst stirred tank bioleaching for copper concentrates processing.

The principle of sustainable development in mining in Zambia calls for integrating economic activity with environmental integrity and social concerns. The importance of a healthy environment to future generations is recognized as a 'pillar' of sustainable development. This entails shifting from conventional techniques to a better method to extract the country's most important resources. Bioleaching is a technology that is sustainable in terms of processing bulky low grade surphide mineral ores using low capital expenditure with minimal environmental degradation effects. Zambia needs to focus its effort on research in bioleaching process and its application as it can contribute significantly to the economic and social development of the country.

Progressive works from this study will focus on investigating the amenability of copper sulphide minerals, from various mines in Zambia to bioleaching. This preliminary leaching kinetics data may be useful for the design, and possible development and operation, of tank or heap bioleaching operations.

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