Review Paper

Biohydrometallurgy and Biomineral Processing Technology: A Review on its Past, Present and Future

Chandra Sekhar Gahan^{1,2}, Haragobinda Srichandan¹, Dong-Jin Kim¹ and Ata Akcil³

¹Mineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Yuseong-gu, Daejeon, 305-350, REPUBLIC OF KOREA

²SRM Research Institute, SRM University, Kattankulathur - 603 203, Kancheepuram district, Chennai, Tamil Nadu, INDIA

³Department of Mining Engineering, Mineral Processing Division, Suleyman Demirel University, TR32260, Isparta, TURKEY

Available online at: www.isca.in

Received 6th September 2012, revised 2012, accepted 2012

Abstract

The Microbial hydrometallurgy and microbial mineral processing of metal sulphides is currently a well established technology. Over past years there has been a huge amount of developments with regards to the understanding of its both engineering perspective as well as fundamental approach with regards to the microorganisms. The huge diversity of the microorganisms, which has come into picture over the years of research and development have made the engineers to go beyond several limitations of working temperature to salt tolerance of the microorganisms in harsh conditions to deliver better technologies for the future operative plants. Today scientists have been able to deliver the various mechanisms involved in bioleaching but still there are facets to be really understood and more importantly on the front how lab scale research can be turned out into full scale operation by scaling up the research and optimizing the engineering aspects of the research. Most of the bioleaching operation has shown their productivity in commercial application of refractory gold concentrates using mesophilic microorganisms followed by the cyanide leaching to recover optimum amount of gold with an environment friendly method compared to the conventional method of roasting. Research in the area of chalcopyrite bioleaching is still continuing o solve the mysteries of jarosite precipitation and formation of passivation layer, which inhibits the copper recovery in a heap leaching of chalcopyrite by biological methods. Use of extreme thermophiles in chalcopyrite bioleaching is making a revolutionary movement to solve the mystery behind the scaling up the process, which could be possible to be solved in future. Bioleaching with other sulphide minerals together with Acid Mine Drainage (AMD) mitigation, which is a serious concern today, is taking is taking shape today in order to cater the needs of the mankind. However the biohydrometallurgy research seems to contribute to a greater extent in framing environmental friendly process with regards to hydrometallurgical operations in future and establish a developed technology to benefit human beings needs by its upcoming research and development.

Keywords: Biomining, refractory gold, copper, chalcopyrite, bioleaching, nickel sulphide, biooxidation, acid mine drainage.

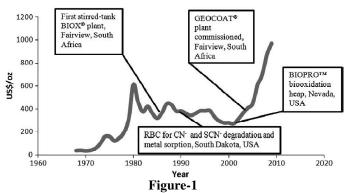
Introduction

The future development with regards to metal demand and supply has motivated the current research and development to emphasize more on the secondary metal resourses like secondary ores and industrial byproducts or waste material generated from various resources. The new technologies for metal production should be novel and economically viable for both the mining companies and entrepreneurs involved in the process. Metal recovery by biological process has emerged as an alternative technology today especially in metals like gold and copper. The last decade has particularly observed the dramatic increase in the metal prices to unprecedented high levels followed by an unparalleled event of declining base metal prices. Rapid increase in production costs, and finally a sustained period of uncertainty in metal prices has developed with time. This change in the metal prices has seriously influenced the global mining companies. The mining industries has always been observing the flip-flop occurring in the metal prices exhibiting cycles of high and low metal prices, which

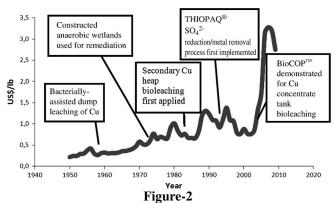
have forced the companies for the contraction of the industries. The decline in the metal prices increases the cost of production and often it is observed that the production is curtailed at times and the mining plans are changed targeting higher metal grades followed by cut off of the research and development expenditures and sometimes lay-offs of research and engineering personnel too. Biohydrometallurgical processes for mine production and metals remediation have lower capital and operating costs than competitive technologies and are therefore economical to implement during mining down-cycles compared to other processes. A comparative analysis was carried out to observe how gold and copper biohydrometallurgical operations took the role with the increase and decline of metal prices over time.

Figures 1 and 2 illustrates the prices of gold and copper, respectively ever since the inception of biomining. The reason for selection of gold and copper is due to the full scale operations of these two metals existing today in various

industries today. The graphic representations show the significant developments in biohydrometallurgy, where it is peculiar to see how these technologies have been under development for a decade or more before actually being put into commercial practice.



Cumulative average gold price (US\$/oz) in actual dollars from 1968 through 2009 with significant biohydrometallurgical applications (reprinted from Brierley, 2010)



Spot average copper price (US\$/lb) from 1950 through 2008 with significant biohydrometallurgical applications (reprinted from Brierley, 2010)

Figures 1 and 2 also suggests that most biohydrometallurgical innovations have been commercially implemented during times of low metal prices, which could be interpreted to mean the mining industry is more inclined to apply biohydrometallurgical processes during leaner times^{1,2}. The BioCOPTM technology was, in fact, demonstrated as the copper price was rapidly increasing. While increasing copper price was unlikely to be the only reason why the technology was not fully commercialized³, it may have been a contributing factor. Metal prices, of course, are not the only motivating factor for employing biohydrometallurgical processes⁴. Other drivers include, the Cost of production — as energy costs escalate, mining, processing, and environmental costs substantially increase. Some biohydrometallurgical methods for processing and remediation are less energy intensive than alternative technologies and can potentially reduce costs for the industry.

Also, biohydrometallurgical processing methods eliminate net Smelter Royalties associated with smelting and refining and potential penalty charges associated with smelting feeds with impurities⁵. Sulfuric acid costs can be volatile depending on demand and location⁶, while the bioleaching can be used in some situations for on-site acid production to eliminate or reduce acid purchases. Exploitation of ore deposits, which are not amenable to conventional processes or otherwise difficult to exploit for example the development of secondary copper sulfide ore deposits, which may be too small or too remote to be economically amenable to making a flotation concentrate either for shipping or onsite smelting. Another example is processing of sulfidic-refractory gold ore properties located in regions where biooxidation technologies may be more suitable for cost and work force reasons. A third example is ores deposits with complex mineralogy, which could be difficult to treat by conventional methods, where biohydrometallurgy could turn out to be a viable alternative technology to go ahead. It can also be reasoned here that this biohydrometallurgical techniques could be a source of maximizing the use of existing infrastructure like the installed solvent extraction-electrowinning plants in copper extraction as bioleaching of copper sulfides allows to use these existing facilities to maximize the use of the existing investments by the industries⁵. The permissions for operating mines by environmental authorities for the effluents generated form the mining could be at times take very long time and difficult too, but use of biohydrometallurgical technology could ease the process for environmental issue over conventional technologies as this process of biological approach is found to be a green technology.

Historical Overview

Starting from the inception of the living world on this earth about 3.8 billion years ago, microorganisms are known to have appeared as the first living organisms when there was no free oxygen with a reducing atmosphere composed of methane, carbon dioxide, ammonia, and hydrogen. The microbial world at that time utilized the available resources like methane or hydrogen for their survival instead of oxygen for their metabolism, which is currently referred as anaerobic metabolism which is 30-50 times less effective compared to oxygenic or aerobic metabolism. Since than throughout the evolution microorganisms have proved to be amazingly adaptable and enable themselves for their existence on this earth starting from warm climatic conditions on the equatorial regions up to the freezing cold climates in the poles. They posses best qualities to adapt in all extreme conditions for which few of them have been classified under the class of Extremophiles comprising of acidophiles, methanogens and thermophillic. Few of them also are very comfortable in pshychrophillic conditions too. Microbes are well known to posses a much potential role in the application of water purification and clearing up after oil disasters and we have always been benefited from their ability to dissolve minerals too.





Figure-3
View of Acid Mine Drainage pollution caused in RioTinto
thriving with acidophiles

With regards to mineral dissolution of the minerals Rio Tinto located in the south west of Spain stands to be one of the remarkable sites with very hostile environment for the mineral dissolving microorganisms. Several researches carried out at Rio Tinto enabled the researchers to compare RioTinto with another planet Mars in our Universe. Rio Tinto located in the heart of the Iberian pyrite belt rich in sulphur has observed natural mining caused by the invisible miners via pyrite biooxidation for thousands of years generating huge amount of acidic water overloaded with several heavy metals in it. The acidic water stream flowing in Rio Tinto can be seen as deep red color (figure 3), which gives an idea regarding its high iron concentration pervading the entire landscape. Due to this highly acidic stream and heavy metal laden water, it has been very difficult to find any vegetation or animals in this region. Microbial studies conducted on the red stream showed the prevalence of millions and millions of microorganism's dominating the ecological niche. But the question that remains unsolved is how do they survive, which is very simple to answer i.e. these microbes thriving in the ecological niche oxidize the pyritic minerals generating the required energy for their survival and replication process. This metabolic phenomena occurring with the microorganism in this environment stands to be a very basic model which can be related to the type of microbes that initiated the progress of life on the earth.

Biomining microorganisms are mostly autotrophic microorganisms, which use iron or sulphur or both as their major energy source and CO_2 as their carbon source unlike to the heterotrophic microorganisms using organic carbon as their

major energy source. These biomining microbes are known to be more comfortable in the acidic environment, infact they need acid, live in acid and they even produce acids oxidizing the pyrite and sulphur for which they are called acidophilic or acid loving. The other thing which is most important of these microorganisms is that they are the Archaea responsible for breaking down or dissolution of the mineral by iron and sulphur oxidation. In other words they are also described as lithotrophs, which means a rock eater as they can actually eat the rocks and this can be easily observed in any mining complex with sulphidic minerals mostly pyritic. Energy rich ore oxidize without bacteria but microorganisms make the process several thousand times faster. Using oxygen form air the bacteria extract the metal from the ore, this releases energy which they use to grow and to multiply. The metals become soluble in water and Rio Tinto was among the first places in the world to exploit this phenomenon which benefited mankind in the later part of the time. The oldest metal object found here takes back to 5000 years. The question still remains unanswered regarding who created them. Historians probably don't agree with these characteristics but they were all Iberians. The next cultures that were established were the Tartessians, because they have several references in Bible and it seems that king Solomon was very fond of their metallurgical potential and later after the Phoenicians, there was lot of wars to dominate this Mining complex, and finally the Romans were there from first century after Christ's death and ruled there for about 400 years with big mining operations. During that period slave Laborers were used to provide the Roman Empire with iron silver, gold and copper. The working conditions inside the mining complex was completely inhuman and harsh, the slaves lived and worked in total darkness chained to rock faces and survived at best for 4 years. After the Romans came the Visigoths than the Spanish. But it wasn't until the end of 19th century, that full scale mining was resumed in response to the huge demand from metals created by the industrialization of Europe. Thereafter the Mines at Rio Tinto were taken over by English, who abandoned Bioleaching in favor of roasting as they could successfully extract same amount of copper in six months compared to long period of 3 years via bioleaching. All extraction methods became more brutal as blasting was used in Open pit mines (figure 4).



Figure-4
View of Open Pit Mines in RioTinto

The open Pit mining is well known to be less environmental friendly because of its high pollution level and destruction of the landscape, which can't be restored by any another means. The metal of interest present in the mineral complex inside the rocks in the mountains is recovered by destroying the big mountain into small pieces instead of finding alternative ways to recover the metal by restoring the nature by preserving the mountains. By removing a mountain we may end up with huge amount of acid mine drainage, which will influence the water table as huge amount of undesirable metals which gets dissolved in the acidic solutions and passes into the water resources like lakes and rivers found nearby the mining complex. This can lead to series of diseases caused by hazardous metal pollution in the water resources. The toxic sulphur dioxide fumes released from the roasting process led to the severe sickness of the miners and also started damage the vegetation surrounding the industrial complex within a radius of 15-20 kms. In the year 1888 both the miners and local farmers had enough to tolerate furthermore and came out for a demonstration against the problems and issues considering their lives at stake. Perhaps this agitation grew so big that it was considered to be one of the world's first proenvironmental demonstrations so far, but unfortunately this demonstrated was forcibly suppressed by the military forces at that time leading to a death toll of about 200 men, women and children. As a thought bioleaching was reintroduced the few years later but the golden era Rio Tinto had it in and the mining operation was soon closed down. Today Rio Tinto and its bacteria is once again attracting interest of an unusual kind.

The bacteria posses a vital force strong enough to survive in outer space became known in 1969. The crew of Apollo 12 had retrieved a camera left behind on the moon by a non man space probe two years earlier. The camera contained perfectly signed individuals of Streptococcus myetis bacteria commonly found in the nose and mouth of human beings. The space scientist were intrigued by the discovery because if such bacteria can survive on the moon, there could be a possibility of existence of a similar forms of life on Mars, a planet quite similar to earth and as they could find a similar condition in Rio Tinto suggest how life emerged on earth. Rio Tinto is considered an interesting and good geological analogue of Mars and the reason is that they start to describe the mineralogy of Mars and in very specific part of Mars called meridianpi has similar mineralogy as found in Rio Tinto produced by biological activity. It has opened window, that there is a place on earth there is this type of biology that produces type of mineralogy obviously gives some connection with Mars and RioTinto. Future space scientists can expose their instrumental conditions in Rio Tinto similar to those in space and these bacteria might just help the biologist solve the mystery of life on Mars, but here on earth the bacteria are already engaged in advancing development with regards to Biomining. Nowadays the metals are so universally employed we take them for granted and the global demand is rapidly increasing. In the west consumption is 10 kg per person a year. The corresponding figure for china is only 2 kg whoever accounts for nearly all of the increased demand for copper. Russia, Brazil, India and Indonesia are also growing rapidly and in great needs of metals. Countries all over the world are literally being hovered for ore deposits. The question is to know how to find new resources and specially to be probably less dependent on the importation of these metals. So there is a new interest in producing metals in Europe because of that due to the pressure that has been now imposed by the environment of the emerging countries and their needs in metals. Europe one of the first centers of the Industrialization and consequently has a very well developed mineral processing fabrication, metal forming business and is one of the world's largest consumers of metals. Europe unfortunately was not as blessed with mineral resources as set in other places in the world like South America, Africa, Australia and most of the easily accessible lower cost higher grade minerals have been depleted today. In Europe there are number of small and medium size ore deposits which still haven't been touched. So far they haven't been considered worth exploiting using ordinary smelting process. Europe also has large quantities of mining waste with the metal content that frequently exceeds that of recently located ore deposits.

Biomining Technology

Biomining is the utilisation of biohydrometallurgy to process metal ores. Biohydrometallurgy is essentially the application of biotechnology to processing minerals. Technically, the process is a branch of hydrometallurgy, but uniquely it involves the use of microorganisms to generate chemical oxidants, such as ferric iron and proton acidity. Biomining can be subdivided into bioleaching and biooxidation operations. Bioleaching involves the solubilisation of an insoluble metal sulfide to a soluble metal, which can be recovered from the leachate. This is most commonly used for the recovery of copper or uranium from low-grade ores. Biooxidation utilises mineral oxidation, but in this case the target metal remains in an insoluble phase. Biooxidation is often used in the pre-treatment of gold concentrates, prior to conventional cyanide-extraction. However, the modern application of biomining was only initiated in the 1960's with the construction and irrigation of heaps for the recovery of copper at the Kennecott Bingham Canyon Copper mine, Utah, U.S.A.⁷. Since the 1980's, there has been a large expansion in the number of heap leaching operations for copper recovery from low-grade ores, with many operations initiated in Chile. Between 1980 and 1998, the amount of the world's copper produced from biomining operations increased from 10% to 25% 8. Biomining was originally seen a means of extracting metals from low-grade ores, tailings and other mine wastes. Initially used for the recovery of copper, since the 1960's it has also been used in the recovery of uranium, and in the mid-1980 was developed for use in the pre-treatment of gold-bearing ores ⁹. The most important of these operations are located in developing countries, such as Chile, Indonesia, Mexico and Peru and Zambia. Many developing countries have significant mineral reserves and mining is often one of their main sources of

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income. Biomining, with its relatively low capital and running costs, is ideally suited to such countries¹⁰.

Since the 1992 Earth Summit in Rio, the concept of sustainable technologies and development has become very popular⁸. Biohydrometallurgical extraction procedures find favour in this respect as they are "almost without exception more environmentally friendly" than physicochemical processes¹¹. While the environmental costs associated with mineral extraction and primary processing, such as ore crushing and to some extent mineral concentration, are comparable, the process does not require the huge amounts of energy expended during roasting or smelting and does not produce harmful gas emissions. Care must be taken with the resulting leach solution, which contains highly elevated concentrations of soluble metals and acidity, as its release into the environment could have serious consequences. However, in the long term, the waste left over from biological processing may be less chemically active.

The longer that the leaching process is continued, the lower the concentration of reactive sulfide minerals left in the resulting waste. This means that the potential for chronic pollution generation through subsequent microbial weathering is reduced. Many metals can be recovered using biomining microbes including, for example, copper from chalcocite (Cu2S), nickel from pentlandite ((FeNi)₉S₈), zinc from sphalerite (ZnS), lead from galena (PbS) and gold via the dissolution of gold-bearing ores such as arsenopyrite (FeAsS), although not all are commercially processed at this time. Biomining processes can be broadly divided into two main types: irrigation-types and stirred tank-types. Irrigation-type processes involve the irrigation of crushed rock with a leaching solution, followed by the collection and processing of the leachate or pregnant liquor solution (PLS) to recover the target metals, commonly by a solvent extraction/electro-winning (SX/EW) process. Stirred tank-type processes use continuously operating, highly aerated stirred tank bioreactors.



Figure-5 View of a pilot scale high temperature heap leaching operation in Mexico

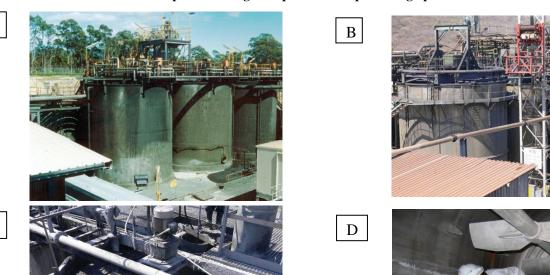


Figure-6
A and B: Continuous stirred tank reactor (CSTR); C: Top view of a CSTR; D: Inside view of a CSTR

 \mathbf{C}

The extraction of metal values from sulphidic ores and mineral concentrates using microorganisms was termed as Biomining. Biomining is the utilization of biohydrometallurgy to process metal ores. Biohydrometallurgy is essentially the application of biotechnology to processing minerals. Technically, the process is a branch of hydrometallurgy, but uniquely it involves the use of microorganisms to generate chemical oxidants, such as ferric iron and proton acidity. Biomining can be subdivided into bioleaching and biooxidation operations. Bioleaching involves the solubilisation of an insoluble metal sulfide to a soluble metal, which can be recovered from the leachate. This is most commonly used for the recovery of copper or uranium from low-grade ores. Biooxidation utilizes mineral oxidation, but in this case the target metal remains in an insoluble phase. Biooxidation is often used in the pretreatment of gold concentrates, prior to conventional cyanide-extraction. In recent years remarkable achievements have been made in developing biomining to cater the interest of the mineral industry to match the global demand for metals in the 21st century. Depletion of high grade mineral deposits makes the traditional pyrometallurgical process uneconomical for metal recovery. The search for alternative metal recovery processes to achieve economical advantage over conventional methods motivated the use of the biohydrometallurgical process, which in turn have accelerated the willingness of the metal industries to use low grade minerals¹². Biomining is mostly carried out either by continuous stirred tank reactors (figure 5) or heap reactors (figure 6). Continuous stirred tank reactors are used for both bioleaching and bio-oxidation processes collectively termed as biomining.

Reasons for the preference of Stirred tank Biooxidation over Heap leaching: Stirred tank biooxidation processes are mostly applied on high grade concentrates for recovery of precious metals like gold and silver, whereas the stirred tank bioleaching process is used for the recovery of base metals like cobalt, zinc, copper, and nickel from their respective sulphides, and uranium from its oxides. Continuous stirred tank reactors are advantageous and widely used due to the following reasons¹³. The continuous flow mode of operation facilitates continual selection of those microorganisms that can grow more efficiently in the tanks, where the more efficient microorganisms will be subjected to less wash out leading to a dominating microbial population in the tank reactor. Rapid dissolution of the minerals due to the dominance of most efficient mineral degrading microorganisms utilizing the iron and sulphur present in the mineral as the energy source. Therefore there will be continuous selection of microorganisms which will either catalyze the mineral dissolution or create the conditions favorable for rapid dissolution of the minerals.

Process sterility is not required, as the objective of this process is to degrade the minerals stating less importance on type of microorganisms involved in it. Therefore, more importance lies on an efficient dissolution process and the microorganisms that carry out the dissolution process efficiently are typically the most desirable ones. Continuous stirred tank biooxidation of refractory gold concentrates and in one case on a cobaltic pyrite concentrate is currently used in more than ten full-scale operations using two different technologies with three more plants coming up in the near future 12,14-17. Several gold biooxidation plants were commissioned over the last 20 years with few new plants commissioned and is progressing fast with rapid industrialization (table 1). Canadian-based BacTech mining company's bacox process is used for the treatment of refractory gold concentrates ¹². Three plants using the bacox process are in operation, with the most recent plant at Liazhou, in the Shandong province of China, owned by Tarzan Gold Co. Ltd^{18,19}. Minbac Bactech bioleaching technology has been developed jointly by bateman and mintek in Australia and Uganda. Recently the BacTech Company has signed an agreement on June 2008, to acquire Yamana Gold in two refractory gold deposits in Papua New Guinea. BacTech Mining Corporation have achieved significantly improved metal recoveries from the test work carried out on the tailing materials from the Castle Mine tailings deposit located in Gowganda near Cobalt, Ontario. This metallurgical work is a precursor to BachTech's plan to build a bioleaching plant near Cobalt, Ontario, to neutralize the arsenic-laden tailings prevalent in this area, and at same time also to recover significant quantities of Co, Ni and Ag present in the tailings. BHP Billiton Ltd operates pilot and demonstration scale processes for the recovery of base metals from metal sulphides of nickel, copper and zinc by stirred tank bioleaching 20. Bioleaching of zinc sulphides has been widely investigated on laboratory scale by various researchers²¹⁻²⁸. The possibilities to process low grade complex zinc sulphide ores through bioleaching have received much attention and have been tested in pilot scale^{25,29}. MIM Holdings Pty, Ltd. holds a patent for a fully integrated process that combines bioleaching of zinc sulphides with solvent extraction and electrowinning of zinc metal³⁰. New developments in stirred tank processes have come with high temperature mineral oxidation, which has been set up in collaboration between BHP Billiton and Codelco in Chile¹².

Stirred tank-type operations involve the processing of mineral concentrates in large bioreactors, and offer much more control than irrigation-based operations and therefore allow superior leaching efficiencies in terms of rates and metal recovery. Aeration, temperature and pH can be continually adjusted to optimise microbial activity in a stirred-tank reactor. These are usually arranged in series, with a continuous flow of material into the first, which overflows to the next, and so on. Retention time in the whole system is set to allow for sufficiently complete microbial-mediated oxidation of the target minerals. The feed usually consists of mineral concentrate, mixed with water to a set pulp density, with a microbial inoculum and additional nutrients. As with other similar forms biotechnological application (such as bioremediation), stirredtank reactors usually offer the most effective (though not necessarily the most economic) level of processing. Most stirred tank operations are employed for the biooxidation of refractory

gold ores; the value of the gold produced displacing the higher capital and running costs required for the implementation of these processes. Conventionally, gold is solubilised from ores and concentrates using cyanide. However, gold ores may be refractory due to the presence sulphide minerals, such as with gold-bearing arsenopyrite ores, which may occlude gold particles from the cyanide solution. In such ores, less than 50% of the gold may be recovered without pre-treatment. Biooxidation is used to disrupt the sulphide mineral matrix, making the gold accessible to the lixiviant. Total gold recovery can be increased to over 95% through the use of such a biooxidation process. Table 1 lists some of the commercial stirred tank biooxidation plants pre-treating refractory gold concentrates. Biooxidation of refractory gold concentrates in continuous stirred tank reactors and bioleaching of copper and nickel via heap reactors are some of the established and commercialised technologies in present day use. Bioprocessing of ores and concentrates provides economical, environmental and technical advantages over conventionally used roasting and pressure oxidation 12,17,31,32

Increasing demand for gold motivates the mineral exploration from economical deposits and cheaper processing for their efficient extraction. Different chemical and physical extraction methods have been established for the recovery of gold from different types and grades of ores and concentrates. Generally, high-grade oxidic ores are pulverised and processed via leaching, while refractory ores containing carbon are roasted at 500°C to form oxidic ores by the removal of carbon due to combustion and sulphur as sulphur dioxide gas. However, the sulphidic refractory gold ores without carbon are oxidised by autoclaving to liberate the gold from sulphide minerals and then sent to the leaching circuit, where gold is leached out using cyanide³³.

In many cases pyrometallurgical processes for the pre-treatment of refractory gold concentrates via roasting have been replaced with continuous stirred tank reactors as a pre-treatment for successful removal of iron and arsenic through biooxidation in the global scenario today. The first biooxidation plant was commissioned in 1986 by Gencor, at the Fairview mine in South Africa. The BIOX® process developed by gencor, operates at 40-45°C and is used by most stirred tank operations¹². In contrast, plants utilising BacTech technology operate at moderately thermophilic temperatures between 45 and 55°C. Several more plants have been built, including a biooxidation plant at Sansu, Ghana. Commissioned in 1994, and expanded since, the plant processes 1000 tonnes of gold concentrate per day, and earns nearly half of the country's foreign exchange¹¹. A commercial stirred tank operation at the Kasese Cobalt Kilembe Mine in Uganda is used to recover cobalt from a 900 Kt dump of cobaltiferous pyritic tailings stockpiled on the site during the mine's operation between 1956 and 1982 (figure 7). The process was developed by the Bureau de Recherches Géologiques et Minières (BRGM), France.





Figure-7
Bioleaching plant at the Kasese mine, Uganda, for extraction of cobalt from pyrite tailings

The plant processes some 245 tonnes of tailings per day, recovering approximately 92% of the cobalt 15,34. The BioNIC® process has been commercialised by BHP-Billiton for the extraction of nickel from low-grade ores, and is based on the BIOX process⁷. Pilot-scale plants in South Africa and Australia have demonstrated the viability of the process, and Queensland Nickel have decided to proceed with a plant aimed at processing approximately 5,000 tonnes of nickel per year³⁵. Biomining using highly aerated, carefully controlled stirred tank bioreactors is highly effective, with mineral decomposition occurring within days rather than weeks or months as with irrigation-type systems. However, due to the level of engineering and process control involved, these are considerably more expensive operations than irrigation-type processes. Efficient aeration is difficult to achieve, and constitutes the largest individual running cost. Another major constraint of these systems is that only approximately 20% pulp densities can be maintained¹². At densities greater than this, efficient aeration becomes very difficult, and shear forces due to the motion of the physically damages the mineral-leaching impellers microorganisms, affecting leaching efficiency.

Table-1
Plants using continuous stirred tank biooxidation for pretreatment of refractory gold concentrates (Brierley, 2010)

Plants using continuous stirred tank biooxidation for pretreatment of refractory gold concentrates					
Industrial plant and location & owner	Concentrate treatment capacity (tons)	Operating years	Current status/Performance/Reasons for closure		
Fairview, Barberton, South Africa/Pan African Resources	62	1986 - present	Gold field's BIOX®		
Sao Bento, Brazil/AngloGold Ashanti	150	1991-2008	Gold field's BIOX [®] . A single-stage reactor was used to pretreat concentrate for pressure oxidation (under care and maintenance)		
Harbour Lights, Western Australia	40	1991 - 1994	Gold field's BIOX®. Ore deposit depleted (decommissioned)		
Wiluna, Western Australia/Apex Minerals	158	1993-present	Gold field's BIOX®		
Ashanti, Obuasi, Ghana/AngloGold Ashanti	960	1994-present	Gold field's BIOX®		
Youanmi, Western Australia	120	1994-1998	BacTech Bacox		
Tamboraque, san Mateo, Peru/Gold Hawk Resources	60	1998-2003	Gold field's BIOX®		
Beaconsfield, Tasmania, Australia/Beaconsfield Gold	~70	2000-present	BacTech Bacox		
Laizhou, Shandong Province, China/Eldorado Gold	~100	2001-present	BacTech Bacox		
Suzdal, Kazakhstan/Centroserve	196	2005-present	Gold field's BIOX®		
Fosterville, Victoria, Australia/North gate Minerals	211	2005-present	Gold field's BIOX®		
Bogoso, Ghana/Golden Star Resources	750	2006-present	BacTech Bacox		
Jinfeng, China/Eldorado Gold	790	2006-present	Gold field's BIOX [®]		
Kokpatas, Uzbekistan/Navoi Mining and Metallurgy	1,069	2008-present	Gold field'sBIOX®		
Coricancha, Peru	60	1998-20008	Gold field'sBIOX® Temporarily stopped (under care and maintenance)		

Heap bioleaching is a rapidly emerging technology for the extraction of base metals from sulfide minerals. Significant attention has been focussed on the development of bioheap leaching in recent years⁷. Heap bioleaching is mostly practiced on low grade copper ores with 1-3% copper and mainly on secondary copper sulphide minerals such as covelite (CuS) and chalcocite (Cu₂S) (figure 8). In heap leaching, the crushed secondary sulphidic ores are agglomerated with sulphuric acid followed by stacking onto leach pads which are aerated from the base of the heap. Then the ore is allowed to cure for 1-6 weeks and further leached with acidic leach liquor for 400-600 days. A copper recovery of 75-95% is obtained within this period of time.

As the construction of heap reactors are cheap and easy to operate it is the preferred treatment of low grade ores ³⁶. Commercial application of bioheap leaching designed to exploit microbial activity, was pioneered in 1980 for copper leaching (figure 8). The Lo Aguirre mine in Chile processed about 16,000 tones of ore/day between 1980 and 1996 using bioleaching³⁷. Numerous copper heap bioleaching operations have been commissioned⁷, since then Chile produces about 400,000 tones of cathode copper by bioleaching process, representing 5% of the total copper production ³⁸. The

Talvivaara Mining Company Plc. (figure 9, 10 and 11) started an on-site pilot heap in June 2005 and the bioheap leaching commenced in August 2005. Talvivaara have started full production since 2010. Production of nickel is approximately 33,000 tones and has the potential to provide 2.3% of the world's current annual production of primary nickel. The first shipment of commercial grade nickel sulphide started in February 2009³⁹.



Figure-8
A: Heap Bioleaching of Copper



Figure-9
Heap leaching operations at Talvivaara

Production process of heap leaching at Talvivaara, Finland

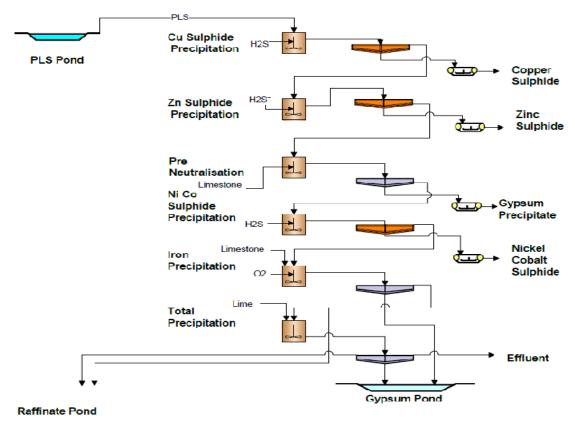


Figure-11 Flow sheet of the down stream processing at Talvivaara, for metal recovery

Heap leaching can be traced as far back as the 1600's in Spain, Germany, Sweden and China ⁴⁰. One of the most notable earlier applications of bioleaching was at the Rio Tinto mines in southwestern Spain. At the beginning of the 1890s, heaps of low grade copper ore were constructed and left for 1 to 3 years for natural decomposition. Although, this practice was maintained

for several decades, the contribution of mineral solubilising bacteria was not confirmed until much later. Reference to iron (II) oxidation by *Acidithiobacillus ferrooxidans* was first made in 1951⁴¹. In addition, in 1961, the leachate at the Rio Tinto mines was found to contain *Acidithiobacillus ferrooxidans*⁴². There was a slow progression to commercial application of

biohydometallurgy (including bioleaching) where activity of micro-organisms would be facilitated. In 1970, Lacey and Lawson reported that the iron (II) oxidation by Acidithiobacillus ferrooxidans was half a million to a million times faster than abiotic chemical oxidation by dissolved oxygen ⁴³. As a result of this and similar work, copper leaching from heaps was initiated in 1980 and several copper heap bioleach operations have been set up since then ⁴². Irrigation-type processes can involve in situ, dump, or heap bioleaching. In situ bioleaching describes the process where metals are solubilised and recovered directly from the ore body itself. This process was employed to recover uranium from low-grade ore at the denison mine, ontario, Canada. In this operation, blasted ore in an underground stope was flooded intermittently with AMD, and aerated. The leach liquor was removed after periods of about three weeks and the uranium recovered. During 1988, this process recovered nearly 350 tons of uranium, at a then value of US\$ 25M^{9,44}. The suitability of such operations is entirely dependent on the local hydrogeology, which must facilitate good leachate recovery without significant loss into the surrounding environment. Loss of leachate to underlying soil, porous rock and groundwater would have a severe environmental impact due to the chemical compositions of these liquors. Dump leaching involves the recovery of metals from dumps of very low-grade mine ores and mine wastes. The Bingham Canyon biomining project in the 1950's is an example of this process; the largest of the dump leaching operations on this site comprised four billion tonnes of low-grade copper waste¹¹. The Bala Ley plant, owned by Codelco in Chile runs a dump leaching operation, where huge quantities of low-grade copper ore are subjected to cycles of preconditioning, irrigation, rest, conditioning and washing. With each step taking up to a year to complete, a single cycle may run for many years.

Heap leaching (figure 12) is similar to dump leaching, but involves the construction of carefully designed heaps of ore, usually of low-grade, in specially prepared areas. The ore is first crushed and then agglomerated, usually with sulfuric acid before being stacked in heaps up to 10 m high on pads lined with an impermeable barrier, such as a high density polyethylene liner. The design of a heap operation may include aeration pipes, added during construction, to allow forced aeration of the heap. A leaching solution, often the raffinate left following metal extraction from the PLS, is used to irrigate the heap from the top. This may or may not be supplemented with inorganic nutrients and a microbial inoculum. The PLS may be recycled to the top of the heap, as an "intermediate leach solution". The heaps are designed with the optimisation of microbial activity in mind, and leaching efficiency is therefore superior to dump leaching operations. Adjustments can be made to the aeration rate, if forced aeration is employed, which may help to control temperature as well as the availability of oxygen and carbon dioxide. Irrigation can be controlled in terms of flow rate and composition, in an attempt to ensure that sufficient nutrients are supplied to the microbial population, without saturating the heap⁷. Table 2 lists some copper heap leaching operations. While heap leaching operations are mainly employed for the bioleaching of copper, a heap leaching operation was constructed for the biooxidation of refractory gold ore by the newmont mining corporation at the gold quarry mine in Nevada, USA. The process utilises a mixture of mesophilic, moderately thermophilic and thermophilic microorganisms, and allows low-grade ore containing as little as 1 g gold t⁻¹ to be processed economically^{11,16}. Heap leaching operations are almost exclusively used to treat graded but unprocessed ores. However, GeoBiotics LLC have developed the GEOCOATTM process, which involves coating inert, support rock with a thin layer of ore concentrate. This process offers much shorter leaching times than standard heap leaching, while avoiding the capital and running cost associated with stirred tank operations. This process is in use at the Agnes gold mine in South Africa⁴⁵.

Irrigation-type processes allow only minimal control over reaction conditions within the rock pile. These processes rely on microbial activities to produce the ferric iron lixiviant ultimately responsible for the extraction of the target metal from the ore. This requires an adequate supply of oxygen and carbon dioxide, which is difficult to achieve in a large heap. Internal temperature is difficult to measure and control, and depends on several factors, including heap height, local climate and irrigation and aeration rates. It is also intrinsically linked to the sulfide mineral content of the rock. The higher the sulfide content, the higher the temperature is likely to become. Internal temperatures between 65-80°C are not uncommon 16,46. Conversely, if the sulfide content is too low, the temperature may not be high enough to allow for sufficiently rapid mineral dissolution, rendering the heap uneconomical. The heterogenic nature of heaps, with steep pH, nutrient and temperature gradients creating different macro- and micro environmental conditions adds the unpredictable performance of the heap as a whole⁴⁷. The BioNIC[®] process has been commercialised by BHP-Billiton for the extraction of nickel from low-grade ores, and is based on the BIOX process'. Pilot-scale plants in South Africa and Australia have demonstrated the viability of the process, and Queensland Nickel has decided to proceed with a plant aimed at processing approximately 5,000 tonnes of nickel per year³⁵. Biomining using highly aerated, carefully controlled stirred tank bioreactors is highly effective, with mineral decomposition occurring within days rather than weeks or months as with irrigation-type systems. However, due to the level of engineering and process control involved, these are considerably more expensive operations than irrigation-type processes. Efficient aeration is difficult to achieve, and constitutes the largest individual running cost. Another major constraint of these systems is that only approximately 20% pulp densities can be maintained¹². At densities greater than this, efficient aeration becomes very difficult, and shear forces due to the motion of the impellers physically damages the mineralleaching microorganisms, affecting leaching efficiency.

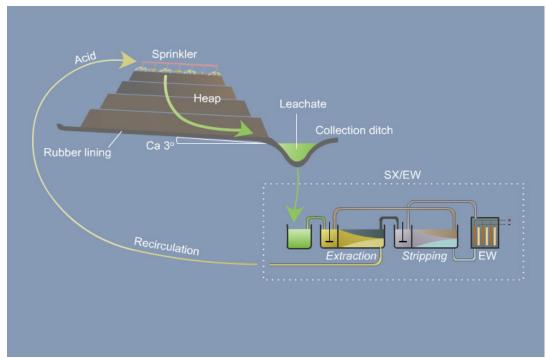


Figure-12 Model of heap leaching process (Reprinted from BiomineWiki)

Table-2 Industrial Copper heap bioleaching operations throughout the world (adapted from Brierley, 2010)

Industrial Copper heap bioleaching operations throughout the world*				
Industrial plant and location/owner	Cathode copper production (tons/year)	Operational status		
Lo Aguirre, Chile/Sociedad Minera Pudahuel	15,000	1980-1996 (Ore depletion)		
Mount Gordon (Formerly Gunpowder), Australia/Aditya Birla	33,000	1991-2008 (On care and maintenance)		
Mt Leyshon, Australia (Formerly Normandy Poseidon)	750	1992-95 (stockpile depleted)		
Cerro Colorado, Chile/BHP Billiton	115,000	1993-present		
Girilambone, Australia/Straits Resources & Nordic Pacific	14,000	1993-2003 (Ore depletion)		
Ivan-Zar, Chile/ Compañía Minera Milpro	10,000 - 12,000	1994-present (currently leaching primary ore)		
Punta del Cobre, Chile/Sociedad Punta del Cobre	7,000-8,000	1994 - present		
Quebrada Blanca, Chile/Teck Resources	75,000	1994 - present		
Andacollo Cobre, Chile/ Teck Resources	21,000	1996 - present		
Dos Amigos, Chile/CEMIN	10,000	1996 - present		
Zaldivar, Chile/Barrick Gold	150,000	1998 - present		
Lomas Bayas, Chile/Xstrata	60,000	1998 - present		
Cerro Verde, Peru/Freeport McMoran	54,200	1997 - present		
Lince II, Chile/Antofagasta Plc	27,000	Closed 2009 (high mining costs)		
Monywa, Myanmar/Myanmar No.1 Mining Enterprise	40,000	1998 - present		
Nifty Copper, Australia/Aditya Birla	16,000	1998 – present (oxide/sulphide)		
Morenci, Arizona/Freeport McMoran	380,000	2001 - present		
Lisbon Valley, Utah/Constellation Copper	27,000 projected	2006 - present		
Jinchuan Copper, China/Zijin Mining Group	10,000	2006 - 2009		
Spence, Chile/BHP Billiton	200,000	2007 - present		
Whim Creek and Mons Cupri, Australia strait Resources	17,000	2006 - present		
Skouriotissa Copper, Cyprus/Hellenic Copper	8000	1996 - present		
Course Privates consultance IIC *Corney down biologals or out		1. Al 70/ . C.l 1.D. 17M C		

Source Brierley consultancy LIC. *Copper dump bioleach operations are not included in this table. About 7% of the world's 17Mt of copper is produced by heap bioleaching. Another 8-13% of the world's copper is produced by dump bioleaching

Future Challenges in Biohydrometallurgy

Commercial challenges: Biomining technologies are mostly developed by mining companies, biotechnology companies, government laboratories, university research scientists and engineers, and mining consultants. The journey from the laboratory research to commercial application of biomining technologies developed by these various organizations faces much more bottlenecks or limitations together with very difficult challenges. The total amount of time required to research, develop, pilot and commercialize the technology, which normally takes at least ten years or more as two decades thereby leading to long-term commitment by Research and development unit with proper cooperation from financial terms and management issues. The biomining site are normally site specific for which every technology developed needs an onsite pilot plant followed by demonstration scale and finally leading to a Full scale operation depending upon the conditions and the results obtained which can be very costly affair. The biomining technology should also be such a feasible technology, which can either outcompete or at par to compete with the existing technology with respect to every parameters taken into consideration by the mining companies. To be specific the bioleaching technology should be able to compete in making required concentrate fulfilling industries requirement at par to pressure oxidation, roasting/smelting, and emerging chemical leaching processes. Similarly metals bioremediation should also be competitive to the existing technology of alkaline precipitation, ion exchange and reverse osmosis, which are used by the industry under special conditions. The rate of success is also another risk factor which needs to be incorporated during the study. The risks involved in commercializing new technologies are detailed by others ^{48,49}. Failure in technology is a common thing for any research organization or mining company but it indirectly hampers the name and fame of the institutions involved in final design and commissioning. The new technologies always requires and urges for a huge capital investment since the process units may need to establish the front-end and the back-end of the actual biomining process. Intellectual property Rights (IPR) is another very important factor as Mining companies often balk at paying licensing fees or royalties for technology due to various reasons like changes in ore type and newer processes negating the value of the technology; licensing fees may stifle business deals, mining companies may be reluctant to open production logs which is necessary to assess licensing fees. Licensing fees or royalties for biomining processes is impossible to negotiate particularly for metal production as it could be many factors which can affect the production, which are not in the hands of the owner. Process guarantees for mine production and environmental biotechnologies is the most difficult part as discussed above. Finally the availability of skilled engineers and scientists is always been a problem lying with mining companies⁵⁰.

Technical challenges: The technical challenges and opportunities faced by research and development units are the

bioheap leaching of primary sulfide minerals despite of few steps have been taken to understand and progress with respect to chalcopyrite^{5,51}. However much more attention has to be given to chalcopyrite biochip leaching to understands the problems faced during the leaching process like reasons for aestivation occurring in heaps due to jar site precipitation and iron hydroxides and which re the jar site formers and the diffusion barriers for the leachant to progress the leaching and more importantly the leaching kinetics and finally how to get optimized conditions suitable for luxuriant bacterial growth and good recovery of copper minerals and economic feasibility. Emphasis should also be given in understanding the fundamentals of the slightly reducing conditions that can occur within the heap when thermophiles are used for dissolution of chalcopyrite and other primary copper sulfide minerals⁵⁰. Presence of silicate minerals bound to the complex polymetallic sulphides has been a big issue in the design of heap bioleaching 51,52. Bioheap leaching model development, integration, and validation developed via heap leaching aspects taking hydrology and heat balance into account need to be given a through thought to understand mathematical modeling aspects to use the process in robust conditions. Other direction which could be looked into lies in better understanding of secondary copper sulfide heap leaching even though the crushed ore heap leaching of secondary copper sulfides has been widely used over a decade lacking some information in production issues. Further addition to all the aspects discussed above a lot of questions lies unanswered like the time taken by the microorganisms prevalent in the bioheap conditions where the source of inoculum is the raffinate together with natural growth of microbes in the stacked ore. Benefits of inoculation of microorganisms in the heap together with extent of aeration requirement in the heap to get better recovery and amount of aeration required. Is the temperature issue important in the heap bioleaching of secondary sulphides and the reasons behind it as slow rate of oxidation of sulfides in the absence of pyrite, which needs to be solved? Finally the microbe-mineral interface interactions followed by mechanisms involving in the heap with respect to galvanic interactions, oxidation-reduction potential, and pH and dissolved metals ion concentration leading to toxic effects on the microbes together with down steam processing issues. In-situ leaching is one of the growing concerns in each and every nick and corner around the world as urbanization have forced human habitation nearby the mining operation which have made it very important to decrease mining foot prints. In-situ mining would drastically decline the impacts of mining on human habitation but this issue needs to be retrospect and efficiently accomplished and is of course a big challenge for mining organizations and tomorrows intellectuals. Technological advancement is required to development sustainable technologies to treat decommissioned cyanideleached heaps by rotating biological contactors by developing methods to treat cyanide-, thiocyanate-, and metal-contaminated waters resulting from gold treatment⁵³. However, the technology has not yet been successful and developed and needs to be evaluated considering various environmental impacts, but Biotechnological approach can lead to a huge cost savings in return. Technology for stabilizing sulfide-bearing wastes is also another aspect to be looked into, which tends to be huge challenge to future biomining professionals.

Biohydrometallurgy Future Prospects

Biomining is going to take a major role both in biohydrometallurgical operations and biomineral processing together with bioremediation as an advantageous technology to deal with the problems and issues related to the rising environmental concerns around the globe. Biomining itself tends to be an economical and technically viable technology for small deposits which are unable to support huge financial crunch involved in the process of extracting metals values and remediating polluted industrial sites. It also offers an opportunity as an auxiliary process for on-site generation of acid for adjunct operations, such as base metal oxide heap leaching, while in some cases might be more feasible taking environmental concerns into act. Though commercial success in certain minerals have been seen for years but technical challenges are huge which is unsolved till date. Emphasis has given to biooxidation pretreatment of sulfidic-refractory gold concentrates in stirred-tank reactors together with dump and heap bioleaching of secondary copper sulfide ores and Nickel sulphides while development is on its way to reach success with regards to heap leaching of low-grade chalcopyrite ores and Uranium oxides ^{5,54}. A huge amount of opportunities still lies in the biomining technology to be fully realized such as bioleaching of zinc sulphides and black shale⁵⁵⁻⁵⁷. Further more to add up with the future is in-situ leaching using microbial processes.

Conclusion

Biohydrometallurgy and Biomineral processing is well known for its application in a variety of base-metal sulphides, mostly either in full scale operation or demonstration scales in various countries around the globe. One of the interesting things observed in his Bioprocessing minerals and metallurgy industry is its environmental friendly process together with economical process. Biohydrometallurgy application especially in case of refractory gold concentrate has been replacing roasting plants in recent years. The replacement of roasting plants in countries like China has shown the progress of biohydrometallurgy as a promising technology for future. Utilisation of bioleaching process for treatment of industrial and municipality waste is also taking its pace slowly and steadily. The use Biohydrometallurgy techniques for the treatment of low grade base-metal dumped at mines site, which are in fact costly to treast by smelters have considered biopprocessing as advantageous process. Sometimes it has been observed that complex ploymetallic ores containing more than one metal values makes the flotation process difficult to produce high value concentrates, therefore bioleaching of several metal values prior to flotation helps the selective preparation oc concentrates.

It is expected that research and industrial developments via heap bioleaching of low-grade primary ores and concentrates together with tank bioleaching and biooxidation makes a greater leap in the technological advancement of Mineral and metal industry in the days to come.

Acknowledgements

Authors are thankful for the research support provided by leading foreign research institute recruitment program through the national research foundation of Korea (NRF) funded by the ministry of education, science and technology (MEST) (2011-00123). Financial support from the research project of the Korea institute of geoscience and mineral resources (KIGAM) and the energy and mineral resources engineering program grant funded by the ministry of knowledge economy, Korea (GP2011-001-2) is gratefully acknowledged.

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