Comparison of Copper Extraction Methods from Aynak Ore Compatible with the Environment

Abstract

The environmental impacts of mining and mineral processing, particularly in developing countries, have been increasing. Mining activities, especially in open-pit mines and the extraction of copper from sulfide ores, generate environmental pollution and acid leakage that harm the ecosystem. Given the abundance of copper in nature and its concentration in sulfide minerals, finding environmentally friendly methods for copper extraction is of particular importance. This study evaluates modern and sustainable methods for copper extraction from the Aynak copper mine, one of the largest copper mines in Afghanistan. This study aims to compare and assess the bioleaching and hydrometallurgical methods as environmentally friendly alternatives to conventional pyrometallurgical (smelting) processes in copper extraction from the Aynak copper ore. This study investigates and compares bioleaching and hydrometallurgical methods with pyrometallurgical processes, evaluating them from environmental impacts and economic efficiency perspectives. The results indicate that biotechnological methods, such as bioleaching, significantly reduce environmental impacts, increase production efficiency, and lower operational costs. In contrast, pyrometallurgical methods are associated with higher environmental issues and costs. Considering the advantages of biotechnological methods, it is recommended that these methods be employed as sustainable alternatives in the extraction of copper from low-grade ores at the Aynak copper mine, particularly in sulfide ores, to create environmentally and economically sustainable development in this sector.

Keywords: copper extraction, Aynak ore, bioleaching, environmental pollution, hydrometallurgy, pyrometallurgy

Introduction

Copper is one of the most widely used and beneficial metallic elements that humans have utilized for centuries. Copper minerals are mostly found in sulfide form, and the type of mineral present in copper ore determines the extraction method from copper mines[1]. Copper extraction from sulfide-enriched minerals, which include copper sulfide and iron sulfide, is carried out through thermal methods (smelting or pyrometallurgy), while extraction from acidic ores is done through hydrometallurgy (leaching). Currently, 80% of the world's copper production is achieved through thermal methods, and 20% through non-thermal methods (leaching)[2]. The annual production of sulfur dioxide during the thermal copper extraction process, and its role in environmental pollution, highlights the urgent need for environmentally friendly methods[3]. Hydrometallurgy as an alternative

Comment [AO1]: The statement, "Copper minerals are mostly found in sulfide form," is lacking some basic information. While many economically viable copper ores are sulfide-based (e.g., chalcopyrite, bornite), significant amounts of copper are also found in oxide forms (e.g., malachite, azurite) or as native copper. I will suggest that you rephrase this sentence again. to smelting has been studied for a long time, and success has been achieved in this field[4]. Copper extraction through either pyrometallurgical or hydrometallurgical methods, or combined processes, has its own specific characteristics[5]. However, none of these developed processes have been completely satisfactory, and therefore, new methods and technologies are still being invented in this area. The use of new technologies and techniques such as bioleaching and bio-oxidation offers an effective way for extracting copper from low-grade ores, gold, and other metal resources, which, in addition to simplifying operations, reduces operational costs and causes fewer environmental impacts.

The direct dissolution of copper sulfide minerals, especially chalcopyrite, using acidophilic bacteria, and the conversion of the produced sulfur dioxide into sulfuric acid, which can then be used to produce chemical fertilizers, are among the advantages of using bioleaching and hydrocopper methods for copper extraction. These methods offer significant benefits compared to other copper extraction techniques.

1. How to produce copper concentrate

The ore extracted from the mine is crushed and ground into fine particles to produce copper concentrate. The fine particles are mixed with water and chemicals in the beneficiation plant and then fed into flotation cells. Air is blown into the cells, creating foam that carries the copper compounds to the surface of the cell. As a result, a concentrate with a grade of over 20% copper is obtained.

2. Copper extraction methods

2.1. Copper Extraction by Thermal Method

In the thermal method, the dried sulfide concentrate is smelted in a furnace. In this stage, a matte layer, which contains iron and copper sulfides, forms beneath the slag layer. The temperature of the furnace is around $|1200-1300^{\circ}C|$. Typically, the copper content in the matte is more than 30%. If the copper present in the slag is significant, it is recovered using an electric furnace; otherwise, it is discarded. The molten copper matte is transferred to a converter, where impurities such as iron and sulfur are removed through air blasting in two stages, and blister copper is produced. (1). In the first stage of air blasting, iron is removed by adding silica. In thermal methods, the sulfur present in the concentrate, which is approximately twice the amount of copper, is converted into sulfur dioxide (SO₂). Therefore, a significant amount of SO₂ is released into the atmosphere annually. To prevent environmental pollution, it is necessary to find a way to prevent its dispersion into the air. For example, SO₂ can be converted into sulfuric acid, which can then be used to produce chemical fertilizers.

Comment [AO2]: "The conversion of the produced sulfur dioxide into sulfuric acid" is inaccurately linked to bioleaching (doi: 10.1042/EBC20220257). Sulfur dioxide (SO₂) is a byproduct of pyrometallurgy, not bioleaching. Bioleaching produces sulfuric acid directly during the bacterial oxidation of sulfides.

Comment [AO3]: For clearer understanding, you may specify that the temperature range may vary depending on the furnace and process, such as flash smelting, where temperatures can be slightly lower due to efficient heat utilization.

Comment [AO4]: The statement "the sulfur present in the concentrate, which is approximately twice the amount of copper" may be incorrect. The sulfur content in concentrates varies significantly, often depending on the mineral composition. Blister copper, with a purity of 98.5%, undergoes sulfur and oxygen removal in two stages using air and natural gas in refining furnaces. It is then cast into anodes for electrolytic refining. After refining, cathode copper with a purity of 99.99% is obtained, which is sold in the form of cathode sheets or, after remelting, as slabs, billets, and wires[6].

Therefore, it can be briefly stated that the production of a large volume of SO_2 gas and the necessity to direct this gas for sulfuric acid production, resulting in increased energy requirements for this process, higher costs, and time consumption for copper extraction, are limitations of copper extraction using this method.

2.2. Copper Extraction by Hydrometallurgical Method

Copper extraction from oxidized ores through the hydrometallurgical method is also possible. In this process, the oxidized tailings produced in copper mines and copper oxide minerals are leached with sulfuric acid. The copper-rich solution is then processed using solvent extraction and electrowinning methods to produce copper cathodes. This method decomposes the copper concentrate and dissolves in reactors with agitation under oxidizing conditions. However, chalcopyrite, the dominant copper mineral, does not dissolve easily in sulfuric acid, so alkaline conditions and high-temperature, high-pressure autoclaves are required to dissolve it. This requirement is considered a limitation of this method[7].

2.3. Hydro Copper Method

The principle of this method is based on hydrometallurgy, with the distinction that leaching is carried out using chloride solutions. Laboratory studies have demonstrated the dissolution of chalcopyrite below the boiling point of water using divalent copper ions (oxidant). Another advantage of chloride solutions is the stability of monovalent copper and elemental sulfur (S), which are obtained through the decomposition and dissolution of the sulfide mineral (chalcopyrite). In sulfuric acid leaching, more energy is saved, as in this process, copper and sulfur are oxidized to much higher degrees, with copper reaching a valency of 2 and sulfur reaching a valency of 6[8].

The Hydro Copper process consists of three main stages:

- 1. Leaching of copper concentrate (leaching, solution purification, and precipitation of Cu□O).
- 2. Copper production (reduction of Cu O, smelting, and casting).
- 3. Chemical production (alkaline electrolysis and chlorine production).

2.3.1.Leaching of Copper Concentrate

Comment [AO5]: "Blister copper, with a purity of 98.5%" may not always be accurate, because the purity levels may vary from 96% to 99% depending on the process used in the reaction.

Comment [AO6]: "Chalcopyrite, the dominant copper mineral, does not dissolve easily in sulfuric acid" is correct, but stating that alkaline conditions are needed for chalcopyrite dissolution may be inaccurate. Chalcopyrite dissolution in sulfuric acid typically requires oxidative conditions (e.g., ferric ions) and may involve bacterial bioleaching, not alkaline conditions. I will suggest the use of "oxidizing conditions, such as the presence of ferric ions or bioleaching processes." instead of "alkaline conditions"

2.3.1.1. Leaching

Copper concentrate (particularly chalcopyrite) is leached using divalent copper in a chloride medium. The leaching process is carried out under normal pressure in three stages, with divalent copper (copper chloride) facilitating the dissolution of copper and other sulfides[9]:

 $CuFeS_2 + 3Cu^{+2} \rightarrow 4Cu^{+} + Fe^{+2} + 2S^{0}$

Ferrous iron is oxidized to the ferric state in air and precipitates as goethite or hematite.

$$0.5H_2O + 0.75O_2 + Cu^{+2} + CuFeS_2 \rightarrow 2Cu^+ + FeOOH + 2S^0$$

Other sulfides present in the concentrate are also decomposed, for example:

$$ZnS + 2Cu^{+2} \rightarrow Zn^{+2} + 2Cu^{+} + S^{0}$$

In this method, the concentrate is leached in a countercurrent solution flow under normal pressure at temperatures between 80°C and 100°C, using tanks and agitated thickeners. In each leaching stage, thickeners are used to separate the liquid and solid phases. The solution beneath the third-stage thickener is the final leach residue, which is filtered and washed in a vacuum belt filter. The filter cake is initially washed with a sodium chloride solution and then with water before being filtered again. The filter cake is placed in water to minimize its chloride content before being discarded. The leaching time for the concentrate is 10 to 20 hours, with a dissolution efficiency of 98%. A major portion of the sulfur is obtained in its pure form, although a small amount is oxidized and converted to sulfite. The solution resulting from the leaching contains 60 to 80 grams per liter of monovalent copper (cuprous) and 10 grams per liter of divalent copper (cupric). By introducing air into the reactors, the pH is controlled between 1.5 and 2.5, and no acids or bases are used. The leaching process is controlled by pH and oxidation-reduction equilibrium. In the first leaching stage, cupric ions are reduced as much as possible with fresh concentrate, with minimal or no air used. In the second stage, the amount of oxidant air and the leaching rate reach their highest levels. If the oxidant air flow rate is too high, it increases the pH, causing copper to precipitate as copper hydroxy chloride, which must be avoided. In the third stage of leaching, a high oxidation-reduction potential is maintained.

2.3.1.2. Solution purification

For copper oxide to precipitate, the solution must have a high level of purity; therefore, solution purification is of great importance. This section includes four

Comment [A07]: "The filter cake is initially washed with a sodium chloride solution and then with water before being filtered again." Washing with sodium chloride to minimize chloride content may contradicts the purpose of the wash step.

Comment [AO8]: "By introducing air into the reactors, the pH is controlled between 1.5 and 2.5, and no acids or bases are used." Air alone cannot directly control pH or oxidize the reactant completely. The pH changes indirectly due to oxidation reactions or dissolution of solids.

stages: removal of divalent copper, precipitation of silver and zinc, lead, and others. The solution purification is carried out using ion exchange, which is performed in sequence.

2.3.1.3. Copper oxide precipitation

The copper present in the solution precipitates as copper oxide by using a sodium hydroxide solution (obtained from the alkaline electrolysis-chlorine section). Copper oxide precipitates in the second reactor in the form of crystals with an average size of 10-20 microns. After precipitation, the copper oxide is filtered with a vacuum belt filter. The filter cake on the belt is washed with water, and the aqueous NaCl solution obtained from the filter is returned to the alkaline-chlorine electrolysis section[10].

 $CuCl_2 + 2NaOH \rightarrow CaO + 2NaCI + H_2O$

2.3.2. Copper Production

2.3.2.1. Reduction of Copper Oxide

The wet copper oxide is transferred from the filter to the corresponding tank for feeding into the rotary furnace, where it is continuously charged using the furnace feeding system. In the presence of a hydrogen-nitrogen flow at a temperature of 400- 500° C, the copper oxide is reduced to metallic copper powder.

 $Cu_2O + H_2 \rightarrow 2Cu_{(s)} + H_2O$

2.3.2.2. Melting of Copper Powder and Casting

Copper powder is melted in an induction furnace, and the molten copper undergoes deoxidation. The surface of the molten metal is covered and protected by a layer of graphite powder. A specialized system directs the copper powder beneath this layer for melting[11].

The obtained copper quality meets the LME Grade 1 standard and is suitable for casting into desired shapes, with the possibility of producing wire through the casting unit.

2.3.3. Chemical Production

In the alkaline electrolysis-chlorine section, chemicals enter and exit in a cycle. Using the NaCl solution, which is introduced from the copper oxide precipitation stage, the required alkaline and chloride materials are produced.

Comment [AO9]: The reaction equation provided for the precipitation of copper oxide, CuCl₂ $+ 2NaOH \rightarrow CaO + 2NaCl + H_2O$, is scientifically incorrect. The reaction should not produce calcium oxide (CaO), as calcium is not involved in this process. Instead, the correct product is copper hydroxide, which can dehydrate to form copper oxide upon heating. Consider the below or the follow: CuCl₂ + 2NaOH \rightarrow Cu(OH)₂ + 2NaCl

On heating, the copper hydroxide can decompose: $Cu(OH)_2 \rightarrow CuO + H_2O$

2.3.3.1. Alkaline Electrolysis – Chlorine

This reaction occurs due to the sodium chloride solution:

$$2NaCL + 2H_2O \rightarrow 2NaOH + CL_2$$

The solution used for electrolysis must have very few impurities, especially magnesium. Therefore, an ion exchange method is employed in the solution purification stage. The produced sodium hydroxide is sent to the copper oxide precipitation section. Chlorine gas is used for the oxidation of divalent copper ions (cupric), and hydrogen is used for the reduction of copper oxide.

2.3.3.2. Oxidation of Copper Solution

Half of the leaching solution of the concentrate enters the oxidation reactor, where, using chlorine gas, cuprous copper is converted into cupric copper.

$$2Cu^+ + CI_2 \rightarrow 2Cu^{+2} + 2CI^-$$

This reaction takes place in two reactors with very fast agitation, and the solution is returned to the leaching section.

Some of the advantages of using the hydro copper method include:

- The unit is integrated and highly automated;
- Environmental and safety considerations are observed;
- Sulfur is in its pure form (S), and no SO₂ gas is released;
- Any type of copper concentrate is acceptable;
- Precious metals, especially gold, can be recovered and extracted.

2.4. Use of the Bioleaching Method

2.4.1. General Principles of Copper Bioleaching

The bioleaching method is a modern, economical, and environmentally friendly technique for extracting copper, especially from low-grade copper ores. Over the past two decades, its application has significantly increased. Numerous studies have been conducted on combining the bioleaching and bio-oxidation processes for the extraction of both copper and gold concentrates, though it has not yet reached practical application[12]. The principle of this method is similar to leaching, but the major difference is that direct dissolution of copper sulfide ores, especially chalcopyrite, with sulfuric acid is not possible. Therefore, in the bioleaching method, thermophilic bacteria like *Thiobacillus ferrooxidans* are used in the leaching phase to

enable the dissolution of chalcopyrite[13]. Afterward, copper is extracted using solvent extraction and electrowinning, similar to the conventional leaching method, to produce cathode copper. To achieve this, the extracted copper ore is crushed to the desired size and mixed with sulfuric acid in agglomeration units to facilitate the agglomeration of fine particles with coarse particles for bacterial action. To reduce moisture levels for proper agglomeration, water or raffinate (a solution obtained from the recycling of electrowinning solution) is added. If the ore is not highly acidic, the acid required for mineral preparation can be supplied from the raffinate solution. Raffinate usually contains a small number of bacteria that oxidize copper. The bacteria are initially applied onto the heap of ore through pipes to convert the sulfide ore into oxide form. The agglomerated and prepared ore is sent to an acid-leaching area, where it is placed on a heap of 10-6 meters high on land that has been flattened or on top of previously acid-leached ore. The air required for the bacterial operation is supplied through plastic pipes with specialized air holes placed on the pad, and the air needed for ventilation below the ore is provided by pressure blowers. A specific amount of bacterial solution is applied onto the pads, where the bacteria convert the sulfide ore into oxide ore, and the ore dissolves in acid. The enriched solution collects at the bottom of the heap and is sometimes returned to the top of the heap for further processing or directly sent to the solution separation stage for copper recovery if the desired copper content is reached. The raffinate solution is returned to the acidleached piles for a second round. The acid leaching time varies for different operations, but ideally, it takes about 200 days for secondary copper ores[14]. The copper recovery and extraction rate in this method is approximately 75-85%.

The optimal temperature, sufficient nutrients for bacterial feeding, adequate oxygen supply, proper ore density, and settling time are key factors for achieving optimal results in the bioleaching process. Studies by Sadowski (2002) on the bioleaching of copper and gold concentrates showed that the process is more effective in the presence of iron ions. The conversion of Fe+3 to Fe+2 indicates the level of bacterial activity, and the presence of various types of sulfides, such as pyrite (at 3%), during the leaching process acts as a catalytic agent in the solution, increasing Fe+3 ions. According to these results, copper recovery of up to 86% is achieved after 13 days with the presence of Fe ions and a small amount of pyrite[15].

2.4.2. Different Methods of Copper Bioleaching

2.4.2.1. Heap Bioleaching

Comment [AO10]: This sentence identifies Thiobacillus ferrooxidans as the key thermophilic bacteria used in bioleaching. Thiobacillus ferrooxidans (now classified as Acidithiobacillus ferrooxidans) is a mesophilic bacterium, not thermophilic. It is widely used in bioleaching but operates at moderate temperatures. For hightemperature applications, thermophilic species like Sulfobacillus or Acidianus brierleyi are more relevant.

Comment [AO11]: "The bacteria are initially applied onto the heap of ore through pipes to convert the sulfide ore into oxide form." Bacteria do not directly convert sulfide ores into oxide ores. Instead, they oxidize sulfide minerals, releasing soluble copper ions into the solution. This is a biochemical process facilitated by bacteria like *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, which oxidize sulfide to sulfate.

This model, on a large scale, is particularly useful as an economic method for acid heap leaching of copper tailings or ores. Some of the features of this method include low operational costs and a low (solution separation/electrowinning) ratio[16].

2.4.2.2. Thin Layer Bioleaching

This method is used exclusively for oxidized ores. Thin layer bioleaching involves the crushing and bioleaching of secondary copper sulfide ores in small heaps[16].

2.4.2.3. Reservoir bioleaching

The first copper bioleaching and its concentrate using reservoir reactors were aimed at achieving faster kinetics. This method, due to its lower recovery from chalcopyrite and its cost-effectiveness compared to continuous smelting, has only been used at a laboratory scale. Bioleaching of chalcopyrite concentrate in the presence of cationic ions such as silver leads to faster kinetics in the experiments and higher copper recovery in laboratory details[17].

Discussion and Conclusion

The mineral processing industry is considered a complementary sector in mining activities. The primary function of this sector is to convert the extracted ore into a concentrate suitable for use in smelting plants and the production of ingots. Generally, the beneficiation process includes stages such as crushing (rock breaking – grinding), classification (screening), gravity separation, magnetic separation, electrostatic separation, filtration, flotation, and leaching. Each of these stages, depending on the type and scale of the operation, utilizes different equipment and operates at varying capacities. The processes often consist of three main branches: input feed, concentrate, and tailings. Furthermore, each stage of the operation has its specific environmental impacts, which typically include water pollution, air pollution, and, in some cases, noise generation. Air pollution occurs during various stages of the comminution process, including crushing and grinding, while water pollution is more commonly observed in the concentration stages. One of the major sources of water pollution is the chemical reagents used during processing operations, particularly in flotation and leaching processes.

In addition to the environmental hazards that can arise during the processing of copper ore, the risks associated with the tailings produced from mineral extraction or the waste materials generated by processing plants, which are also significant challenges in mining, should not be overlooked. The accumulation of these materials in the environment leads to the occupation of large areas, and over time, exposure to air causes subsequent consequences. Therefore, utilizing environmentally friendly

biotechnology, such as bioleaching, along with the other solutions outlined in Tables 1 and 2 for processing the Aynak copper mine, which has been contracted and is about to begin its operational phase, will not only result in energy and economic savings but also prevent adverse environmental and economic impacts in the later stages of production.

In Tables 1 and 2 below, the environmental impacts at different stages of copper processing are examined, along with solutions to prevent them.

Prevention Methods	The environment being polluted	Chemical composition	Pollutant stage	Stage name
Use of Scrubber systems			Dust	Crusher (Jaw - Cone)
Use of cyclones, fabric filters, and feed sprinkling	Air	Manganese Mercury		Mill
		Antimony		
		Chromium		
		Nickel	Dust	
		Arsenic		
		Selenium		
		Cadmium		
Installation of cyanide- sensitive and display systems in the heap and transportation pathways.	Surface water, groundwater, and surrounding land.	Sulfuric acid	Acid leakage from acid transfer pipes and the liners used in the heap structure.	Magnetic separation (high current for hematite and low current for magnetite).
Installation of ventilation systems on tanks.	Air	H_2S	Exhaust gas from tanks	Flotation (Fatty acid: collector, Pine oil: frother, Sodium silicate: activator, Sodium hydroxide: conditioner).
Using centrifuge systems to separate fine organic particles	Surface and groundwater	Base metals, precious metals, and organic materials.	Waste (sludge)	Agglomeration.
Installing appropriate filters at the chimney outlet.	Air	SO_2	Exhaust gases from the furnace.	Purification.

Table 1: Analysis of Dust Generated at Different Stages of Copper Processing

Table 2: Environmental issues of mineral processing operation stages

Pollution control and reduction methods	Environmental issues	Section Name	Unit name
Installation of ventilation systems	Emission of gaseous vapors (SO□, HCN) from leaching tanks	Reservoir Leaching	
Control of leaching tanks based on existing standards	Leakage of leaching solution from the tank body		
Storage and handling of chemicals according to existing standards	Contamination of the workplace or chemical storage due to leakage or spillage of the leaching solution		
Transfer of wastewater to the tailings dam	Wastewater production (uncharged solution)	Solvent Extraction - Electrowinning	
Recycling of Used Resins	Used Resins		Leaching
Installation of display systems and sensors for leach solution leakage in heap structure, the proper groundwork for the heap	Infiltration of leach solution into the underlying soil layers and contamination of the area's water resources		
Moistening the area during heap construction	Dust emission during heap construction operations		
Control of heap facilities at specified times	Leakage of leachate transfer pipes to the heap and soil contamination	Heap Leaching	
25	Destruction of the area's structure due to heap construction Release of used pipes and	ricap Leaching	
	liners after the heap's life cycle in the area		
Planting suitable vegetation cover on the heap	The production of a large volume of tailings after the heap's life cycle ends		

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