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Copper ore Leaching with alternative agents

Bachelor Thesis

by

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Abstract

In copper processing, copper bearing sulfide minerals in porphyry deposit that can be efficiently processed by the froth-flotation cells then recovered by smelter. Copper mainly occurs in porphyry deposit with gold, silver and molybdenum. Most currently, research interest has moved to the processing low-grade, oxidized, complex ore bodies and flotation tail from copper processing that contains impurities including silica, iron, arsenic which forms the crud which negatively influence downstream processes like solvent extraction of hydrometallurgical plant. The conventional sulfuric acid for leaching low-grade copper oxidized ores is inefficient in the treatment of the proposed ore contains gangue metals and minerals like iron, silica, aluminum and carbonates results in increased reagent consumption and increased operating costs. In addition to these technical challenges, the use of sulfuric acid impacts on environment negatively including vaporization and contamination of ground water.

Nowadays, in Mongolia the metallurgical plants like 'Achit-Ikht' LLC recover cathode copper by using heap leaching based on diluted sulfuric acid from cut-off grade Cu-Mo ores. Sulfuric acid is very reactive and corrosive. It is soluble in water and ethyl alcohol. Its strong reactivity may ignite organic material. Sulfuric acid will exist as particles or droplets in the air if released to the atmosphere. It has moderate chronic toxicity to aquatic life which has been reported to form stable complexes with copper, iron and other silicate materials. Glycine is a non-toxic, stable, environmentally benign reagent which has been reported to form stable complexes with copper and gold. Also, it is available in bulk industrial quantities. Somehow, using sulfuric acid in industrial scale is harmful for the environment. So, in the research the opportunities to replace the conventional reagent by the new reagent like alkaline glycine solution for reducing toxicity to environment and reducing leach stream recycling cost.

In this research, glycine will be investigated as a potential lixiviant for low grade Cu-Mo ores at alkaline pH. And conventional leaching reagent like diluted sulfuric acid will be studied as reference for comparing metallurgical results with glycine system. Although alkaline glycine solutions have been reported to selectively leach copper over gold from a copper-gold ore, the leaching behavior of the copper ore which is assumed as cut-off grade ore for flotation process

(called 2nd dump of Erdenet mining company) in alkaline glycine solutions would be investigated. In Mongolia, cut-off grade ores have not been leached in the proposed lixiviant system as glycine leaching system in order to establish the influence of process variables on copper. Furthermore, lack of data has been published on the recovery of copper from alkaline glycine leach system on oxidized cut-off grade ore. Due to corona crisis, this research will present potential results of leaching behavior tests from assumptions by help of the literatures.

Using an alkaline glycine solution, has initiated significant interest in using the new technology in various environments such as in situ, dump, heap, vat and agitated tank leaching. That is why, in plan of the research, low-grade copper ore of the 2nd dump of Erdenet mining company will be leached in column leaching and bottle roll under ambient conditions at laboratory scale. Also, the experiments in various conditions will be carried out under various parameters with oxidant as hydrogen peroxide such as various pH values, glycine concentrations and flow rates etc. On the literature noted that copper-gold ores leaching in alkaline glycine solution revealed that, Cu and Au simultaneously leach from both ore types. However, Cu leaches faster than gold. In this research, the literatures revealed that, with the exception of copper oxide minerals leach more rapidly than their sulfide counterparts.

Copper extractions from low-grade copper ore were 25 %, 31.8 %, 36.18 % after 72 hours at initial concentration of glycine 2 Gly : 1 Cu, 4 Gly : 1 Cu, 8 Gly : 1 Cu molar ratios respectively in 500 ml leach solution. After 72 hours, the result of sulfuric acid-based bottle roll test was 61.8 % of Cu was extracted in initial concentration of sulfuric acid with molar ratio of sulfuric acid to pure copper is equal to 2:1. The heap leaching behavior tests results are assumed directly from literatures. For example, 0.5 M concentration of glycine was used in column leaching test on flotation tail from copper-gold processing, the flow rate of leach solution was 0.86 L / h. The result showed that 53.6 % of copper was extracted after 48 days of column glycine leaching test. 3 g / L diluted sulfuric acid was used in another column leaching test on oxidized low-grade copper ore, the flow rates of the leach solution were 0.906 L / h, 2.724 L /h and 1.702 L / h. The result showed that the test with highest flow rate had the highest metal extraction 40 % after only 15 days. Also, the test with the lowest flow rate showed the lowest metal extraction with 28 % of Cu after 15 days.

All in all, the leaching behavior of various glycine-based and sulfuric-acid-based systems will be reviewed, followed by metal extraction over time where economics merit. The result of research will be revealed that advantages and disadvantages of each leaching systems that is based on comparison of economic merit, metallurgical results and environmental effects.

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1. Introduction

1.1 Background of this study

Currently, the mining sector is developing much faster day by day while the high metal content reserves are being declined over time. The copper, gold and other metals concentrate are generally produced productively by froth-flotation from the high metal content reserves. For example, Erdenet Mining Corporation produces 530.0 thousand tons of copper concentrate and around 4.5 thousand tons of molybdenum concentrates annually (EMC, n.d.). Afterwards, the concentrate is recovered by smelter to produce final product as pure metal. Mentioned above is common flow for recovering pure metal technique using pyrometallurgical method. Most copper production in the world is covered by this method.

Before every mining start, elemental and mineralogy analyses are carried out to determine which layer is economic merit for operation and which layer cannot make the profit, on the proposed deposit. Usually upper layers or overburden mixtures are considered to cut-off grade ore for the processing steps like flotation cells due to its high content of impurities. Extracted the overburdens and upper layer minerals (oxidized) mixture ore with low-grade metal ores are dumped as a waste for processing of metal plant. Based on sustainable development rules, to reuse, reduce and recycle the waste like dumped ores, the hydrometallurgy background applies on that oxidized cut-off grade ores to make waste into profit. Hydrometallurgical treatment for the oxidized low-grade ore consists of three main steps including leaching, solvent extraction and electrowinning processes.

More than 20% of copper in the world is produced by hydrometallurgy. The best leaching technique for low-grade copper ore is usually leached with diluted sulfuric acid. Sulfuric acid-based leaching method has been the most extensively applied method for the recovery of copper from cut-off grade ores for over a century. This is because sulfuric acid forms very stable complexes with copper and is relatively selective leading to high copper recoveries. Sulfuric acid is the world's largest volume industrial chemical. The main use is in the production of phosphate fertilizers. It is used to manufacture explosives, other acids, dyes, glue, wood preservatives, and automobile batteries.

When leaching the low-grade ore with diluted sulfuric acid, the sulfuric acid is a reagent that shows that it reacts with other gangue metals and minerals such as iron, silicate minerals, acid consuming minerals. The crude /medium/ is formed when pregnant leach solution act with organic matter /in solvent extraction/ which causes loss of organic matter. Moreover, it acts negative influences to processing operations of plant such as the stirring process, electrowinning and leach solution irrigation systems of dump leaching. All mentioned challenges above cause high operating costs due to manpower and reagent consumption.

In addition to the challenge of sulfuric acid-based leaching system to treat copper ores, sulfuric acid toxicity is a health and environmental concern. A vaporization of acid, acid drainage to ground water, toxic ponds that is dangerous for the habitants has been extensively reported on (leach, n.d.)

The development of an alternative process to sulfuric acid-based leaching system should be considered for the health and environmental issues. So, to decrease the environmental pollution and health hazard, the new technology that leach the base metals with alkaline glycine solution will be further studied.

In the case of metallic copper, its interaction with amino acids (especially glycine) has been extensively reported in the electronics industry and biological systems, but such interactions are yet to be considered in the mining industry (where the copper is mineralized as oxides and sulfides). it has been shown that glycine acts as a chelating agent, rapidly forming irreversible complexes with copper ions oxidized by the peroxide. In a similar manner, the interaction between copper ions and proteins in biological systems has been established to be through the formation of coordinate bonds between copper and the functional groups on amino acids (Tanda, 2017).

From the understanding that a prospective lixiviant for copper leaching should be cheap or recyclable, selective, non-toxic and suitable to downstream recovery processes, glycine presents itself as a potential candidate to partially replace sulfuric acid in the copper dissolution. Glycine is the smallest amino acid with the formula NH_2CH_2COOH. It is sweet tasting crystalline solid with a solubility of 25 g / 100 ml at 25°C. Toxicology information on glycine via MSDS reports show that is not toxic to humans or to the environment. It is used in food, pharmaceuticals and animal feed. Glycine can be synthesized industrially from chloro-acetic acid and ammonia. While glycine can be decomposed by some micro-organisms or destroyed by strong oxidants, it is stable in the water stability band in the pH–Eh diagram at alkaline pH in the anionic glycinate form. Glycine has a high solubility in water of around 250 g L−1 at 25°C, a density of 1.607 kg t^{-1}, molar mass of 75.07 g mol^{-1} and a melting point of 233°C (Chemeo, 2016).

Copper minerals, such as oxides (cuprite), native copper and various sulfide (chalcocite, bornite, covellite and chalcopyrite) can be effectively dissolved from a gold-copper gravity concentrate in the presence of alkaline glycine and an oxidant at room temperature (Oraby EA, 2014). Subsequently it was also shown that various copper oxides (cuprite, malachite, azurite and chrysocolla) can all be dissolved in alkaline glycine, although copper extraction from chrysocolla tends to be poor compared to the other oxide minerals (Tanda BC, 2017). It also showed that the copper glycinate species can be effective measured in alkaline solutions using UV-visible spectrometry.

Although alkaline glycine solutions have been reported to leach copper from a float concentrate and copper minerals specimens, no studies have been done on the leaching behavior of low-grade copper ores like 2nd dump of Erdenet Mining Corporation. This bachelor thesis work was therefore studied to understand the effect of process conditions and variables on the leaching of copper from low-grade copper ore using alkaline glycine solutions and heap leaching behaviors.

1.2 Objectives and significance of this study

The main aim of this bachelor thesis work is to achieve the following objectives:

- To investigate and establish the leaching behavior of low-grade copper minerals in the alkaline glycine solutions by using bottle roll tests
- To study the effects of process variables and impurities in the dissolution of copper from copper ores under glycine solution. /various initial concentration of reagent, hydrogen peroxide and pH/

- To investigate and establish the heap leaching behavior of low-grade copper minerals in the alkaline glycine solutions by using column leaching test.
- To study the effects of glycine leach solution concentration and flow rate of leach solutions in column leaching tests.

The main significant outcomes would be:

- To introduce an environmentally benign process for treating various types of copper ores.
- To enable treatment of ores which fall below cut-off grades for conventional processes.
- To compare new reagent glycine with conventional reagent sulfuric acid by dissolution rate and dissolved impurities.

1.3 Hypothesis

The bachelor thesis work consists of two main experiments such as leaching behavior of low-grade copper ore tests and heap leaching behavior of low-grade copper ore tests.

1. The leaching behavior of low-grade copper ore experiment will be carried out all in the bottle on bottle roller. It consists of main three tests including effect of initial concentration of leach glycine solution test, effect of initial pH value test and effect of hydrogen peroxide as oxidant test. Additionally, sulfuric acid will be investigated to make sure the comparison test of glycine and sulfuric acid leaching. In the bottle roll experiment's expected outcomes are as follows:

   - By increasing its glycine leach solution concentration, metal recovery would increase over time
   - With higher content of hydrogen peroxide as oxidant tests would have more dissolution rate
   - Low amount of impurities would dissolve in the glycine leach solution
   - Alkaline glycine has lower dissolution rate than diluted sulfuric acid on the low-grade copper ore

2. The heap leaching behavior of low-grade copper ore will be carried out in eight columns. Generally, the experiment consists of two main tests including the heap leaching behavior under alkaline glycine solution test and heap leaching behavior under sulfuric acid test which will be performed under different concentrations of leach solutions. Column leaching experiment's expected outcomes are as follows:

    - The test with higher concentration of leach solution will have higher metal recovery
    - Heap leaching dissolution rate would be lower than bottle roll leaching dissolution rate
    - Glycine-based heap leaching test has lower metal recovery than sulfuric acid-based heap leaching test

2. State of the art

2.1 Chapter objective.

This chapter reviews the available literature on the various aspects with regard to the integrated bachelor thesis work. The thesis work aims to propose and study a new leach process by using a new lixiviant for low-grade copper ores and comparison with conventional leach process. First review the potential of copper ores as a major source of future copper. Also, influence of variation of copper on ore processing and copper process will be reviewed.

Selecting the lixiviant for the leach process depends on the ore structure and mineralogy, leaching techniques and environmental management. The properties and characteristics of a good lixiviant for selecting good leaching agent for a purposed ore will be considered.

For copper processing, copper leaching its different methods and chemical formula related to the bachelor thesis work will be reviewed.

All in all, proposing the main lixiviant as glycine for leach process is the new technology. To get understood of the new agent, the chapter will provide the physical and chemical properties of glycine establishing it as a candidate for the leaching of copper from the its ore.

2.2 Copper resources and mineralogical variation of copper ore

Porphyry copper deposits are the largest reservoirs of copper in the upper crust. The copper minerals are mainly existing in porphyry deposits. "*The quantity of undiscovered copper resources is postulated to be about twice the discovered with the mean total of undiscovered resources for porphyry deposits being 3500 million tons "* (Survey, 2014). Porphyry deposits are providing about 60 % of the global copper consumption, the deposits are one the biggest source for metal extraction processes. Even though, porphyry deposits contain millions of tons of ores, metal grades are only averagely less than 1 % of copper.

In Mongolia, the porphyry copper deposits commonly spread throughout at northern and southern. For calling the porphyry copper deposits are Erdenetiin-Ovoo, Saran-Uul, Tsagaan suvarga and Oyu-Tolgoi (J.Byamba, 2009). The low-grade copper ore were investigated at the experiment that received from Erdenetiin-Ovoo Cu-Mo porphyry deposits.

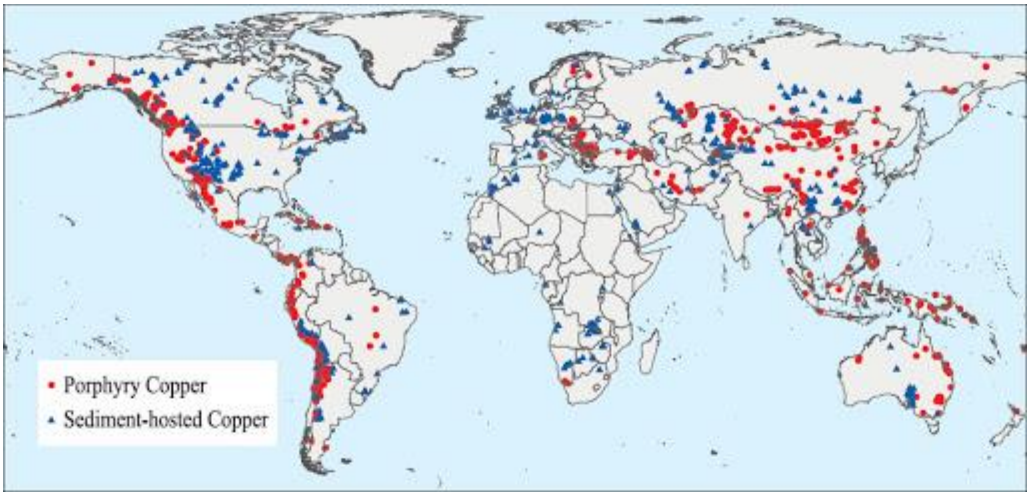
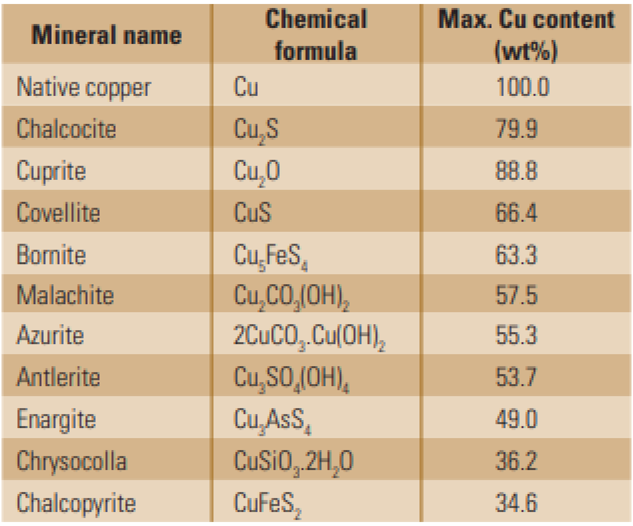


Figure 1 /Mineralogical World distribution of porphyry copper deposits (Johnson, 2012)/

Mineralogy of the ores and feature are important factors that influence for the determination of mineral processing methods and techniques. The influencing factors that from a disparity in metal grain size distribution, mineralogical mode of copper occurrence, host and gangue mineral types.

Table 1 /Common copper mineral chemical formula/



Mineral name	Chemical formula	Max. Cu content (wt%)
Native copper	Cu	100.0
Chalcocite	Cu_2S	79.9
Cuprite	Cu_2O	88.8
Covellite	CuS	66.4
Bornite	Cu_5FeS_4	63.3
Malachite	$Cu_2CO_3(OH)_2$	57.5
Azurite	$2CuCO_3.Cu(OH)_2$	55.3
Antlerite	$Cu_3SO_4(OH)_4$	53.7
Enargite	Cu_3AsS_4	49.0
Chrysocolla	$CuSiO_3.2H_2O$	36.2
Chalcopyrite	$CuFeS_2$	34.6

For example, the influence of textual variation and gangue mineralogy of a porphyry ore on the recovery of copper was reviewed by (Cropp, 2013). They stated that seven key mineralogical factors:

1. The fine-grained copper minerals
2. Locked minerals in composite particles
3. Surface coating on valuable minerals
4. Gangue composites
5. Entrained gangue
6. Activated gangue

7. Deleterious element distribution control the flotation recovery of copper from porphyry ores.

The supergene zone at the top of most porphyry deposits consist of an upper oxidized layer referred to as the cap and an underlying sheet-like zone called the blanket zone. The cap is composed of Cu oxides, Cu carbonates, Cu sulfates, Cu chlorides, Cu silicates and native Cu while the blanket are mostly secondary copper and iron sulfides such as chalcocite, covellite, bornite, and remnants of chalcopyrite (Petruk, 2000). The type of leaching agent and methods are depending on the ore type. For oxidized copper ores are suitable to leach under sulfuric acid. But the ore contains high acid consumption gangue ores like carbonates and silicates, sulfuric acid leaching becomes more uneconomical. So, such ores containing high acid consumption gangues are leached under alkaline lixiviants including ammonia. Copper sulfide minerals like chalcopyrite and covellite are more difficult and slower to be leached under mild conditions. It requires more aggressive conditions like strong oxidizing agents, high temperature and pressure.

2.3 Processing of copper.

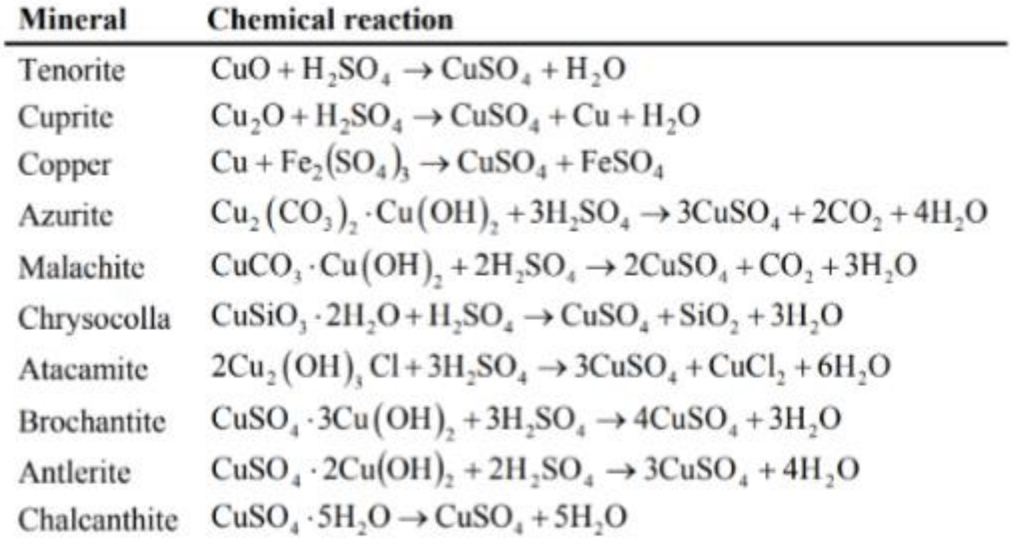
World copper production is provided by generally two main processing sectors including pyrometallurgy and hydrometallurgy. Copper is recovered for its economic value through grinding, flotation and smelting. The gold as byproduct is produced from smelting and refining process of copper. In copper ore processing plant, the copper ore considered as cut-off grade which dumped used to recover the copper by hydrometallurgical routes includes leach, solvent extraction and electrowinning. The most economical approach for sulfide ores has been to produce a copper flotation concentrate for metal recovery by smelting (Dunne, n.d.).

2.3.1 Copper leaching

Leaching is the term applied to the process of extracting a metal from an ore by a solvent, and the removal of the resulting solution from the undissolved portion. It is, therefore, the extraction of a metal from an ore by a wet process. For the copper leaching, conventionally sulfuric acid is used as leach solution also called lixiviant to extract the copper from the ore. Leaching of copper ore can be carried out including heap leaching, dump leaching, in situ leaching and vat leaching etc. The different methods are selected based on its economical merit and mineral composition. Where silicate, carbonates and other gangue minerals has no economic value, it poses serious problems to the conventional diluted sulfuric acid leaching of copper by consuming reagents and negatively affecting the downstream processes. For example, leach solution sulfuric acid reacts with gangues over time, it causes the formation of contamination in pregnant leach solution. The consequence of the formation forms crud /medium/ that detrimental influence on the further processes like solvent extraction and electrowinning. So, the medium should be removed from the solution that cost the man power and causes the reagent lost. The mentioned factors that increases the operating costs for such unit operation.

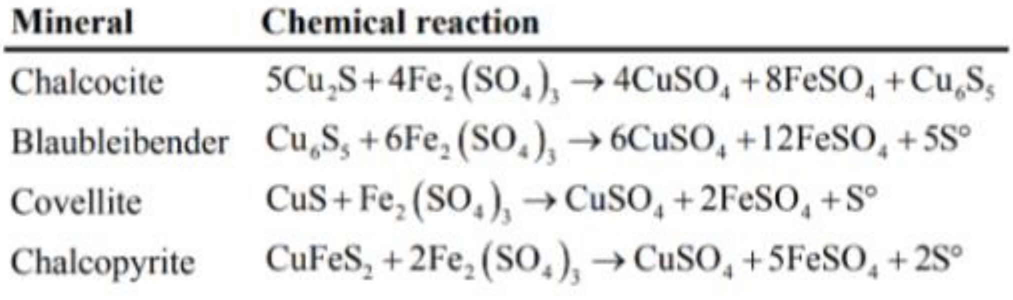
2.3.2 Chemical reactions in conventional copper leaching processes

Table 2 /Copper oxide mineral leaching chemical formula (Sukhbaatar.B, 2019)/



Mineral	Chemical reaction
Tenorite	$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$
Cuprite	$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$
Copper	$Cu + Fe_2(SO_4)_3 \rightarrow CuSO_4 + FeSO_4$
Azurite	$Cu_2(CO_3)_2 \cdot Cu(OH)_2 + 3H_2SO_4 \rightarrow 3CuSO_4 + 2CO_2 + 4H_2O$
Malachite	$CuCO_3 \cdot Cu(OH)_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + CO_2 + 3H_2O$
Chrysocolla	$CuSiO_3 \cdot 2H_2O + H_2SO_4 \rightarrow CuSO_4 + SiO_2 + 3H_2O$
Atacamite	$2Cu_2(OH)_3Cl + 3H_2SO_4 \rightarrow 3CuSO_4 + CuCl_2 + 6H_2O$
Brochantite	$CuSO_4 \cdot 3Cu(OH)_2 + 3H_2SO_4 \rightarrow 4CuSO_4 + 3H_2O$
Antlerite	$CuSO_4 \cdot 2Cu(OH)_2 + 2H_2SO_4 \rightarrow 3CuSO_4 + 4H_2O$
Chalcanthite	$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 + 5H_2O$

Table 3 / Copper sulfide leaching chemical formula (Sukhbaatar.B, 2019) /



Mineral	Chemical reaction
Chalcocite	$5Cu_2S + 4Fe_2(SO_4)_3 \rightarrow 4CuSO_4 + 8FeSO_4 + Cu_6S_5$
Blaubleibender	$Cu_6S_5 + 6Fe_2(SO_4)_3 \rightarrow 6CuSO_4 + 12FeSO_4 + 5S^\circ$
Covellite	$CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + S^\circ$
Chalcopyrite	$CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^\circ$

Table 4 / Impurities dissolutions chemical formula in copper leaching (Sukhbaatar.B, 2019) /

Mineral	Chemical reaction
Pyrite	$FeS_2 + (1-6\beta)Fe_2(SO_4)_3 + 8\beta H_2O \rightarrow (3-12\beta)FeSO_4 + 8\beta H_2SO_4 + (2-2\beta)S^\circ$
Calcite	$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O + CO_2$
Siderite	$FeCO_3 + H_2SO_4 \rightarrow FeSO_4 + CO_2 + H_2O$
Limonite	$Fe_2O_3 \cdot 3H_2O + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 6H_2O$

2.3.3 Heap leaching

The **figure-2** shows that heap leaching process of copper can briefly described in hydrometallurgical single loop. Heap leaching is applied for valuable metals recovery from cut-off grade ores that has been deposited on a prepared lined pad constructed using synthetic material. Before depositing the ores, first they underwent the comminution processes for particle size reduction. The leach solution spread on the top of ore and transfers through ore body by gravity. This process is carried slowly and might last for several day up to 600 days for some sulfide minerals (Mellado, 2009). From a prepared lined pad, pregnant leach solution comes out and feed the recovery plant to recover the pure metals like copper.

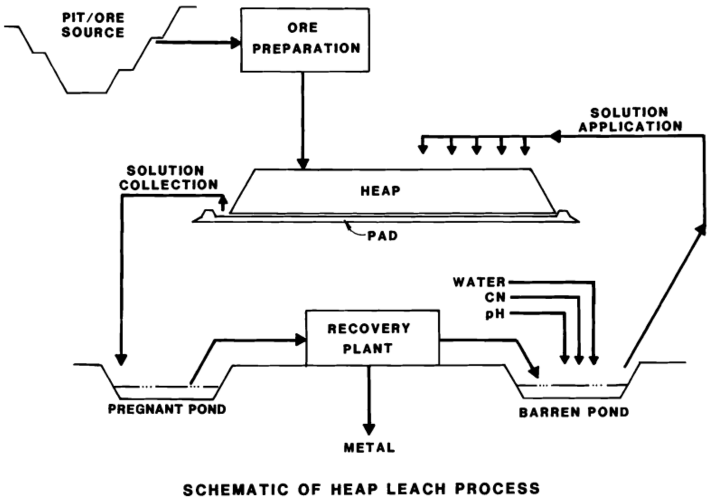


Figure 2 /Simplified figure of heap leaching technique and leach solution recycle streams (911, 2017)/

2.3.4 Dump leaching

The dump leaching is generally applied to run-of-mine which contains very small amounts of valuable metal that is uneconomical to treat by any traditional leaching method. It uses natural terrain which can be steep-sided valleys or hillside to enhance drainage. Copper dissolution process is done by the leach solution that sprinkled on the top of the dump by sprayer with help of pumps. Damp is dissolved and pregnant leach solutions comes out from bottom for recovering the pure cathode copper. The **figure-3** shows the dump leaching method.

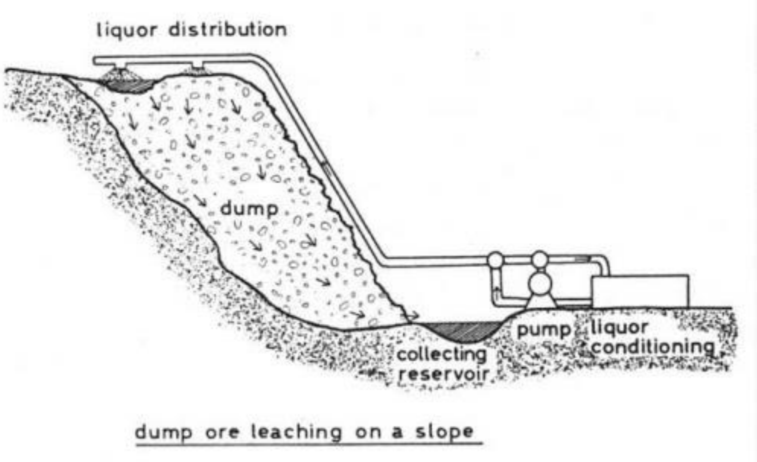


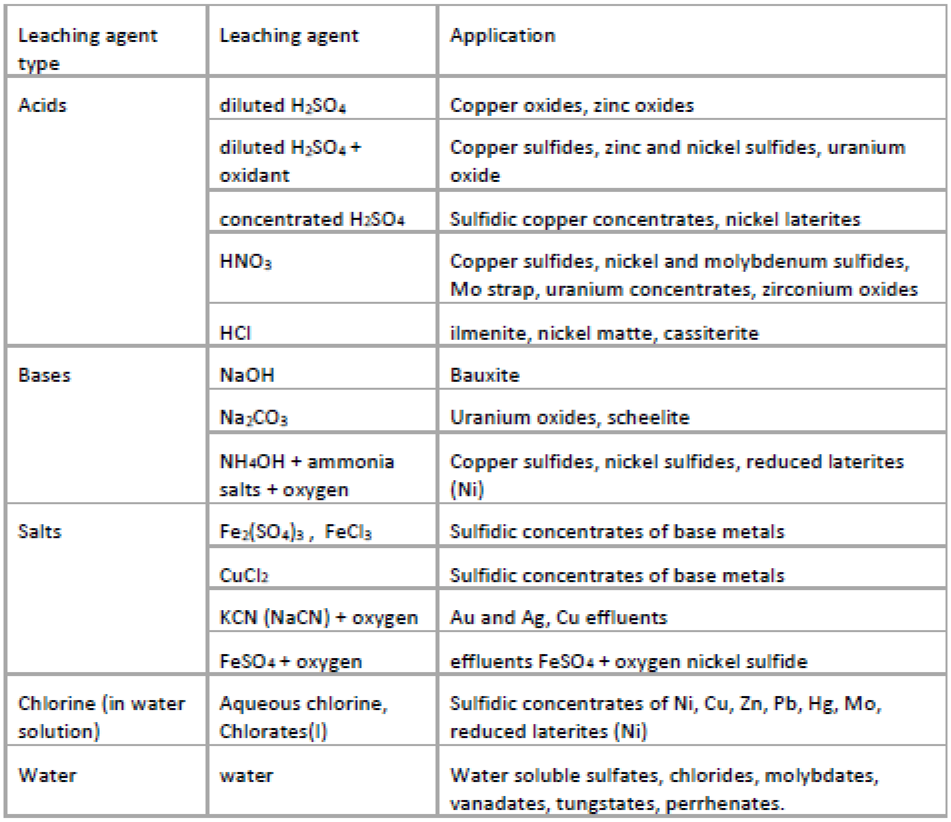
Figure 3 /Simplified figure of damp leaching technique (Näveke, 1986)/

2.4 Characteristics of good lixiviant

The first step of hydrometallurgical processing of mineral that leaching is the most important unit operations for economic and technical success for entire industry. The main objective of leach process is to maximize the valuable metals in the leach solution with desired characteristics. For selecting leach solution, mineralogical composition of the proposed ore is the most significant. According to (Olubambi, 2006), the selection of optimum technical and economic routes for minerals requires a complete knowledge of the ore, especially its chemical and mineralogical compositions, relative amounts of minerals, and particle size distribution.

The sulfuric acid is the most commonly used for dissolution of minerals because of its low cost, availability and low volatility as well as high chemical stability in aqueous solutions. On the other hand, other use of acids like nitric and hydrochloric acid has undesirable aspects including high cost, volatility, corrosiveness and indiscriminate gangue dissolution (Burkin, 2001). The **Table-5** show the commonly used leaching agents and their applications.

Table 5 /Common leaching agents and their application (Tanda, 2017)/



Leaching agent type	Leaching agent	Application
Acids	diluted H_2SO_4	Copper oxides, zinc oxides
	diluted H_2SO_4 + oxidant	Copper sulfides, zinc and nickel sulfides, uranium oxide
	concentrated H_2SO_4	Sulfidic copper concentrates, nickel laterites
	HNO_3	Copper sulfides, nickel and molybdenum sulfides, Mo strap, uranium concentrates, zirconium oxides
	HCl	ilmenite, nickel matte, cassiterite
Bases	NaOH	Bauxite
	Na_2CO_3	Uranium oxides, scheelite
	NH_4OH + ammonia salts + oxygen	Copper sulfides, nickel sulfides, reduced laterites (Ni)
Salts	$Fe_2(SO_4)_3$, $FeCl_3$	Sulfidic concentrates of base metals
	$CuCl_2$	Sulfidic concentrates of base metals
	KCN (NaCN) + oxygen	Au and Ag, Cu effluents
	$FeSO_4$ + oxygen	effluents $FeSO_4$ + oxygen nickel sulfide
Chlorine (in water solution)	Aqueous chlorine, Chlorates(I)	Sulfidic concentrates of Ni, Cu, Zn, Pb, Hg, Mo, reduced laterites (Ni)
Water	water	Water soluble sulfates, chlorides, molybdates, vanadates, tungstates, perrhenates.

To select the suitable leaching reagent should consider the following factors (Avraamides, 1982):

1. It should be selective and have high activity to dissolve components of interest rapidly enough to make commercial extractions possible
2. It should be inexpensive with the possibility to be produced in bulk industrial quantities
3. Compatible with downstream recovery process and also recyclable
4. Environmentally friendly

2.5 Glycine as copper lixiviant

Glycine is called aminoacetic acid that is the simplest amino acid having a hydrogen atom as a side chain, H_2N-CH_2-COOH.

Glycine properties are as follows (Tanda, 2017, p. 38)

- Colorless, sweet crystalline solid in pure form,
- Soluble in water (25g /100ml at 25 C), acids, alkalis but not soluble in organic solvents
- High melting point of 262 C and decomposition point 292 C

Industrial applications of glycine (Drauz, 2000)**:**

- Taste enhancer and sweetener in food production industries
- Buffering agent in cosmetics
- Chelating agent in crop production for cationic micronutrients and also as a fertilizer source
- Pharmaceuticals and medicine in intravenous injections

Aqueous chemistry of glycine (Tanda BC, 2017)

Glycine occurs as an amphoteric agent in aqueous solution acting as an acid and base depending on solution pH. Below the pH of 2.35, the glycinium cation $^{+}H_3NCH_2COOH$ (H_2L) is predominant. The zwitterion $^{+}H_3NCH_2COO^{-}$ (HL) is stable at pH of 2.35 - 9.8. $H_2NCH_2COO^{-}$ (I) is predominant at above pH of 9.8.

Aqueous Chemistry of copper and glycine

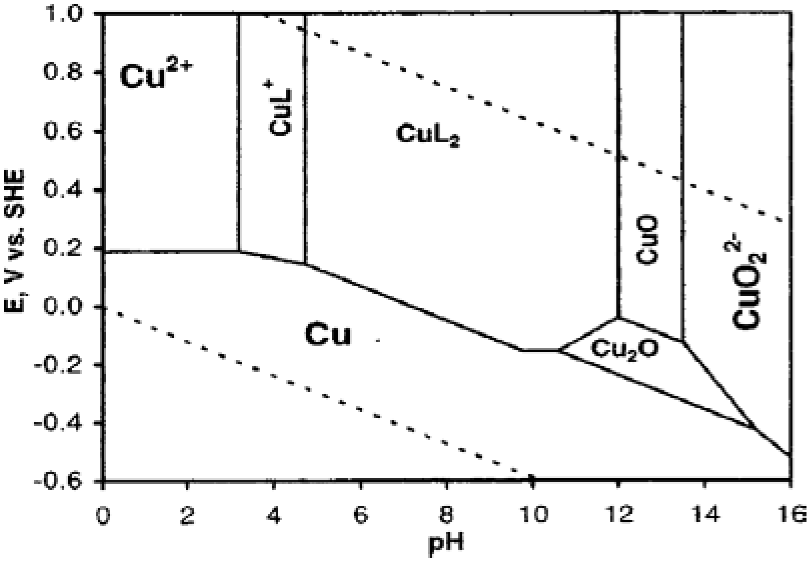
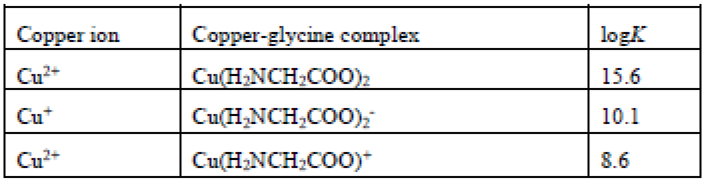


Figure 4 /Eh-pH diagram for copper-water-glycine system at a total dissolved copper activity of 10^{-5} and total glycine activity of 10^{-2} at 25 C and 1 atm (Aksu, 2003)

/Table 6 /Copper glycine complexes and their stability constants (Aksu, 2001)/



Copper ion	Copper-glycine complex	logK
Cu^{2+}	$Cu(H_2NCH_2COO)_2$	15.6
Cu^{+}	$Cu(H_2NCH_2COO)_2^{-}$	10.1
Cu^{2+}	$Cu(H_2NCH_2COO)^{+}$	8.6

3. Materials and method

3.1 Chapter objective

A variety of materials and research methods have been consumed to establish the aim of this thesis. The main objective of this chapter is hence to give a detailed description of the materials, procedures, and analytical techniques that were employed in this research.

With the dominant intention of investigating the leachability of low-grade copper ores in a new leach process and conventional leach process, ores and minerals samples used for all experimentation are described, therefore the methods for sample characterization and preparation for experiments. The ore underwent a variety of leach tests including bottle roll leaching test and column leaching test. The equipment and conditions used for these experiments are detailed in this chapter. Glycine and Sulfuric acid as the main lixiviant in this study and other reagents used for the different experiments are listed in this section as well.

All in all, this chapter explains the basics of different techniques that were carried out to collect the data needed in the leaching experiments. The experimental conditions, parameters and different procedures for samples preparation, low-grade copper ores leaching in bottle roll, column leaching are described in the following sections.

3.2 Materials and Reagents

All reagent used in each experiment were of analytical grade. For preparation of main lixiviants like alkaline glycine solution and diluted sulfuric acid, de-ionized water was used. To prepare main lixiviant alkaline glycine solutions, based on molar ratio of glycine with copper molar weight was considered. A list of the analytical grade reagents and gases used in different experiments described on **Table-7**. **Table-8** also show a list of phase compositions of low-grade copper ore from Erdenetiin-Ovoo deposit.

Based on working cooperation between GMIT and “Achit-ikht” LLC, 500 kg low-grade copper ore was received from 2nd dump of Erdenet Mining Corporation from “Achit-Ikht” LLC. The samples were taken from slope side of dump. However, ore of slope side of dump is less affected by diluted sulfuric acid than irrigation of leach solution area, it might contain the sulfuric acid. The ore was been dumping for 30 years and oxidizing for 30 years. 2nd dump of EMC contains 0.32 % copper. Weight of dump is approximately 56 million tons. Pure copper reserve is considered as 174000 tons. The composition of 2nd dump consists of 25 % of primary copper ore, 50 % of secondary ore and rest of 25 % is oxidized ore.

Table 7 /List of different analytical grade reagents and gases used in this study/

№	Reagent	Chemical formula	Purpose	Purity
1	Glycine	H_2NCH_2COOH	Main lixiviant	AR
2	Sulfuric acid	H_2SO_2	Main lixiviant	AR
3	Sodium hydroxide	$NaOH$	pH modifier	AR
4	Lime	$Ca(OH)_2$	pH modifier	Industrial grade
5	Hydrogen peroxide	H_2O_2	Oxidizing agent	AR
6	Oxygen	O_2	Oxidizing agent	Industrial grade
7	Air	-	Oxidizing agent	Atmospheric

Table 8 / Copper ore type composition in 2nd dump (Byambajav.E, 2020)/

Type of copper mineral	Copper mineral in dump %					
	1984-2000 year		2001-2004 year		Average	
Oxidized copper ore	0.05%	16.92%	0.02%	7.29%	0.05	15.64%
Secondary copper ore	0.18%	55.38%	0.13%	54.78%	0.17	56.03%
Primary copper ore	0.09%	27.69%	0.09%	37.93%	0.09	28.34%

3.3 Equipment and apparatus

3.3.1 Jaw crush, Cone crush and ball mill

Under comminution processes for sample preparation, jaw crusher, cone crusher and ball mill were used to provide the leaching experiments by ore with optimal particle sizes. A half ton sample received from “Achit-ikht” which contains several big particles like 200 mm – 300 mm. Firstly, the sample was crushed into $P_{100}< 38mm$ by jaw crusher as primary crusher. Maximum standard inlet for feed particle size of the GMIT's jaw crusher is 150x125 mm. The maximum allowable particle size for feeding the jaw crusher is 100 mm. Also, crushing size is adjustable ranging between 6 to 38mm. 25 kg of ore from total ore weight of leaching behavior experiments was crushed into $P_{80} < -6$ mm by jaw crusher. Then, the crushed ore was crushed again with roll crusher into $P_{80} < -1$ mm. Finally, the ball mill was used as a milling process. After milling process, the ore was ground into $P_{80} < -75$ micron. The apparatuses are shown in **Figure-5,6,7.**

Figure 5 /Jaw crusher/

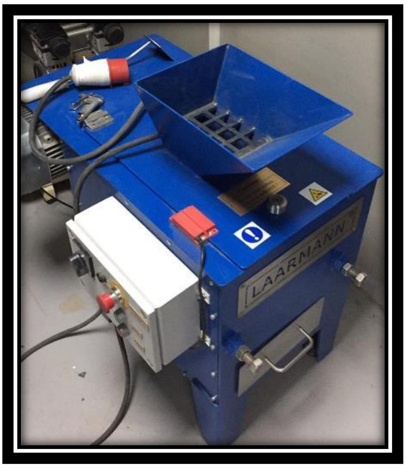


Figure 6 /Cone crusher/

Figure 7 /Ball mill/

3.3.2 Sieving apparatus

The apparatus, is made of stainless steel, was used for sieve analyses to check ore's uniform distribution of particle size on column leaching tests and to check the $P_{80} < 75$ micron of ore for bottle roll tests. The sieve analysis used sieve sizes of 12.5 mm, 8 mm, 4 mm, 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm and 0.63 mm. And the analysis helped to plot the Gates-Gaudin-Schumann graphs for evenly distribution of particle size. Sieving apparatus is shown in **Figure-8**

Figure 8 /Dry-sieve apparatus/

3.3.3 Bottle roller and bottle

The main purpose of this device to determine rapidly leaching the conditions and leaching behavior by using rotation motion in bottle with help of bottle roller. The ore was loaded to the 8 L bottles that are made of polyvinyl chloride cylindrical /PVC/ to carry out the experiments. The loaded bottles were placed on the bottle roller rotating at 100 rmp. To provide that enough oxygen flow was available for the leaching reaction, the bottles were capped with lids having a centered 2.5 cm in diameter hole. The all experiments were carried out in parallel for 72 hours. Several intermediate samples were collected at constant duration ranging for all experiments. For instance: for collecting the samples, let the bottler roller stop and allowing to stand for 5 – 10 min for solid to partially settle. Then withdrawing 3 ml sample and filter it by vacuum filter.

Figure 9 / 8 L bottle and bottle roller /

3.3.4 Leaching column

8 leaching columns were used for determining leaching behavior of low-grade ore in heap. The columns are made of polyvinyl chloride cylindrical (PVC) which has low investment cost and long-lasting life. The less ore loading capacity of PVC columns than transparent columns, allow to start up different columns leaching experiments with around 41 kg of ore. The dimensions of the PVC leaching columns are measuring of 200 mm diameter, 1500 mm of height.

To set up the column leaching experiments, crushed, washed and dried quartz was placed at the bottom of the column for support. Thickness of the quartz was 150 mm. Just above the loaded quartz thickness, discharging outlet was made for pregnant leach solution out. Also, preventing from corrosion of the base of the columns that is made of steel, PVC 8 lids were investigated at bottom of the PVC columns. The ore was then added to the PVC columns and glass wool was placed on the top of the loaded ores to assist in the homogeneous distribution of leaching solution. 8 peristaltic pumps were used to deliver the leaching solution on the top of the columns. The leaching solutions percolated through the ore body by gravity force. Then it discharged at outlet and collected in the pregnant leaching solutions tank. The experiments were considered as without recirculation of the reagent. Thus, 2 tanks were used. One was for pregnant leach solution and another one for feeding leach solution. The samples were collected at 12 pm every day during the 30 days column leaching experiments were carrying out.

By measuring the height of the loaded ore in the column was about 1000 mm.

Figure 10 /PVC- leaching column/

3.3.5 Peristaltic pump

The main role for peristaltic pumps was to feed the leaching solutions from leaching solution tank onto the top of the column loaded by low-grade copper ore. From observation for pumps, the flow rates are not stable at all. So, the flow rates of each solution were measured at 12 pm every day. If the any change of flow rate appeared, with the help of volumetric flask with time dependence, flow rates were measured then the peristaltic pumps were calibrated into the purposed flow rates of leaching solutions. The purposed flow rates for heap leaching tests were 10.25 l / h / m^2 and 16.4 L / h/ m^2.

Figure 11 / Peristatic Pump /

3.4 Experimental procedures

3.4.1 Sample preparation

In the leaching experiment, the cut-off grade copper ores were investigated. A half ton of ore was received in GMIT laboratory from a part of Erdentiin-Ovoo deposit from “Achit-Ikht” LLC. The particle size of the sample was too coarse. So, low-grade ores were crushed into P_{80}< -38 mm by Jaw crusher. After crushing process, for uniform distribution of copper minerals and gangues for both leaching experiments, the samples were mixed well by using shovel. Well evenly intermixed main ore was divided into 4 parts by using coning and quartering method. In order to take the sample which can represent the entire ore body, one-fourth part from the ore was subdivided until 5 kg by coning and quartering method. 5 kg of ore was assumed as representative ore and analyzed for determining head assays in entire low-grade copper ore at laboratory/XRF/. XRF determine the elemental composition of the mineral sample. Therefore, rest sample /around 80 kg/ from one-fourth part was restored for emergency use when the one of experiment fails or mass loss occurs.

Sample preparation for bottle roll test

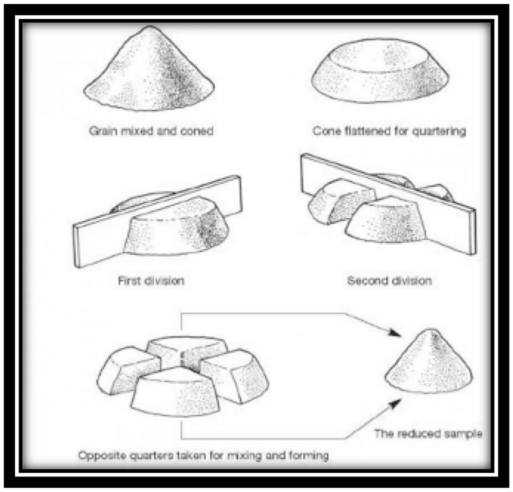


Figure 12 /Coning and Quartering method/

Three-fourths of initial ore /approximately 415 kg/ was investigated for bottle roll tests and column leaching tests. To reduce the error for uniform distribution of copper and gangue minerals, the sample was mixed again and divided into 8 parts by using coning and quartering method. Around 4000 g samples, that are assumed the particle sizes are uniformly distributed, were taken from each part for investigating bottle roll tests. In other word, 32 kg /P_{80} < -38mm/ of sample was used for the experiment. Before feed the bottle roll tests, a cone crusher and ball mill were performed to ground the sample into P_{100} of 75 microns. Coning and quartering method is shown in **Figure-2.**

Column leaching test sample preparation

Rest samples that divided into 8 parts /P_{80} < -38mm/ were loaded in the 8 columns. Before loading the samples, for checking the particle size distribution is uniform or not, 2 kg of samples were taken from 8 parts and sieved individually. In each column, around 41 kg samples were loaded.

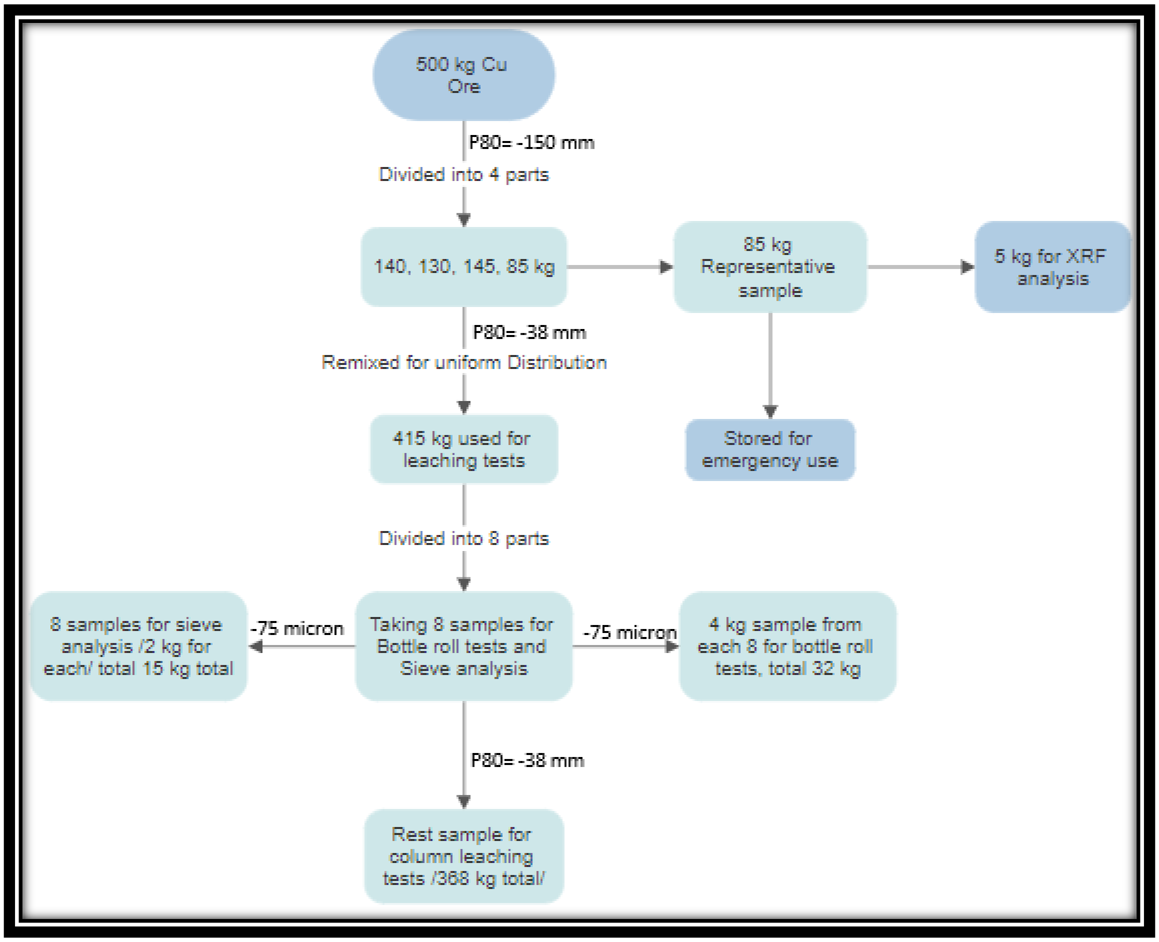


Figure 13 /simplified figure of sample preparation/

3.4.2 Leaching behavior of low-grade copper ore in bottle roll test

Main purpose of this experiments is to study leaching behavior of copper cut-off grade ore in different conditions including various pH values, different reagent concentrations and additive under ambient temperature and pressure. The reason why the bottle and bottle roller were carried out in the leaching experiments is that the method can rapidly determine the effect of conditions by carrying out simultaneous experiments (up to 9 experiments at same time). Main two kind of solutions used in these leaching experiments as lixiviants were prepared from reagent grade glycine and sulfuric acid. Hydrogen peroxide was used

Figure 14 /8 L bottle/

for oxidizing agent. Sodium hydroxide was used for solution pH adjustment. All experiments conducted with 8 L cone bottles, shown in **figure-14**.

The required mass of low-grade ore was weighted to give the equivalent of 2.0 g total copper in the low-grade copper ore. The low-grade ore contains 0.32 % of copper in solid phase. Mass of cut-off grade ore for the experiments was approximately 667 g. The weighted sample was loaded in the bottles and the leaching solutions (Glycine and Sulfuric acid) and additives added. The experiment was started by immediately placing the bottle with sample and 500 ml leaching solutions onto a bottle roller rotating at 100rpm. To provide that enough oxygen flow was available for the leaching reaction, the bottles were capped with lids having a centered 2.5 cm in diameter hole. The all experiments were carried out 3 times, due to decrease the error in results, for 72 hours.

The leaching behavior determining experiments using bottle roller consist of 4 tests including investigation of effect of glycine initial concentrations, investigation of effect of pH values, investigation of effect of strong oxidant and optimization of sulfuric acid concentration for comparison. For investigation of effect of glycine concentration tests, the concentration of glycine was consumed as molar ratio with copper molar weight. For instance concentration of glycine 2 Glycine : 1 Cu is equal to 75.067 g/mol * 2 = 150.134 g / mol per 63.55 g / mol. In our case, in the ore 2 g of copper was investigated. So, concentration of glycine is 4.725 g.

During running of the leaching experiment, several intermediate samples were collected and time ranges for sample collection were 2, 6, 12, 24, 48 and 72 hours. This involved stopping the bottle roller, allowing to stand for 5 – 10 min to allow the solids to partially settle, and then withdrawing 3 ml of slurry samples and filtering it by vacuum filter. The filtrates were analyzed by AAS. **Table-9, 10, 11 and 12** show the bottle roll leaching tests were carried out with different conditions for determining leaching behavior of low-grade copper ore.

Table 9 / Test-1, Effect of initial glycine concentrations tests on low-grade copper ore /

Investigation of Glycine Concentration							
№	Name	Particle size	Peroxide %	Glycine Concentration	pH	Cu Content, 2g	Weight of Ore
1	Test-1	< 75micron	0.5	2 Gly : 1 Cu	11	2 g	667 g
2				4 Gly : 1 Cu			
3				8 Gly : 1 Cu			

Table 10 /Test-2, Effect of initial pH values tests on low-grade copper ore/

Investigation of pH values							
№	Name	Particle size	Peroxide %	Glycine Concentration	pH	Cu Content, 2g	Weight of Ore
4	Test-2	< 75micron	0.5	4 Gly : 1 Cu	9	2 g	667 g
5					10		
6					11		

Table 11 / Test-3, Effect of initial hydrogen peroxide contents tests low-grade copper ore/

Investigation of hydrogen peroxide							
№	Name	Particle size	Peroxide %	Glycine Concentration	pH	Cu Content, 2g	Weight of Ore
7	Test-3	< 75micron	0	4 Gly : 1 Cu	11	2 g	667 g
8			0.5				
9			1				

Table 12 / Test-4, Comparison test with sulfuric acid leaching on low-grade copper ore/

Optimization of sulfuric acid concentration						
№	Name	Particle size	Sulfuric acid Concentration, 2 sulf : 1 Cu	Peroxide, %	Cu Content, 2g	Weight of ore
10	Test-4	< 75micron	3	0	2 g	667 g

From these tests, leaching behavior of low-grade copper test under different lixiviants consists of 30 experiments including 3 repeated experiments. The collected samples from each experiment was 30 * 6 = 180 for determining copper concentration in pregnant leach solution by AAS.

The metal recovery results of each test were obtained from assumption by using the (Tanda, 2017) data of copper extractions from individual copper mineral specimens including cuprite, chalcopyrite and chalcocite etc.

3.4.3 Heap leaching behavior of low-grade copper ore in leaching column

Laboratory heap leach experiments are commonly completed using leaching columns. Column leaching in the laboratory scale, with or without recirculation of leaching solution, simulates percolation leaching operations due to conditions are similar to those in the heap. The column is considered as the center of the heap with same conditions for air and irrigation of lean leaching solution. The experiment can provide useful information about various operating parameters. Such as: particle size, concentration of reagents, mineral composition, flow rate of the acid irrigation systems etc.

Heap simulation experiments were performed parallel in 8 columns for 30 days without recirculation. Because gangue minerals like silicate and carbonate minerals react with sulfuric acid that causes acid consumption. Even though the alkaline glycine solution less reacts with gangue mineral, for good comparison of conventional and new leaching method. The column leaching test with alkaline glycine solution was investigated without recirculation.

Ranging of 41 - 46 kg of low-grade ores /P_{100} < 38mm/ were loaded in each column. For checking uniform particle size distribution, 2 kg of samples from each column were sieved. To get understand of leaching behavior in heap under conventional and new methods with different flow rates including 16.4 L/ h/ m2 and 10 L/ h/ m2. 4 columns were used for carrying out the column leaching experiment under diluted sulfuric acid. Another 4 columns were investigated for performing the column leaching experiment under alkaline glycine solution. **Table-13** and **Table-**

14 show column leaching experiments with different parameters under glycine and sulfuric acid-based system.

Table 13 /Column leaching tests under alkaline glycine solution on low-grade copper ore/

Optimizing flow rate on Glycine leaching							
№	Name	Particle size	Peroxide %	Glycine Concentration	pH	Ore weight	Flow rate
1	Column 1, 2	< 38 mm	1	0.1 M	11	41 kg	16.4 L/ h/ m2
2	Column 3, 4			0.5 M	11		16.4 L/ h/ m2

Table 14 /Column leaching test under sulfuric acid leaching solution on low-grade copper ore/

Optimizing flow rate of Conventional leaching						
№	Name	Particle size	Peroxide %	Glycine Concentration	Ore weight	Flow rate
1	Column 5, 6	< 38 mm	1	3 g/L	41 kg	16.4 L/ h/ m2
2	Column 7, 8			6 g/L		16.4 L/ h/ m2

During 30 days of the column leaching experiment, several intermediate samples were collected and duration ranges for sample collection from pregnant leach solution were at every 12 pm for each day. And involving withdrawing 25 ml of liquid samples from pregnant leach solution tank and filtering it by vacuum filter. Atomic absorption spectroscopy apparatus was used to analyze the filtrate to determine concentration of copper and iron ions in filtrate at laboratory. The total number of samples for ASS analysis were 8 * 30 = 240 samples.

The experimental data were supposed to taken from these planned tests. But, due to quarantine of corona crisis, column leaching data were observed directly from literatures (Tanda, 2017) and (Sukhbaatar.B, 2019).

4. Result and discussion

4.1 Chapter objectives

The main objective of this chapter is to study the leaching behavior and heap leaching behavior of low-grade copper ore in alkaline glycine solution and diluted sulfuric acid at ambient temperature and atmospheric pressure. The comparison of new method with conventional method in bottle roll test, mineralogical phase compositions, dissolution of impurities and particle size distribution for column leaching tests were discussed in this chapter.

The effect of reagent concentration, pH and oxidizing agent were investigated for bottle roll tests. The tests had the limitations such as oxidation /only air through the hole on taps/, pressure and temperatures could not be controlled. However, such experiment cannot cover the determination and optimization of the operating parameters in real system, it can rapidly generate the results like leaching behavior in different leach solutions and effects of different conditions. Low-grade copper ore of 2nd dump EMC from 'Achit-ikht' was consumed.

In addition, the column leaching tests were investigated to determine the heap leaching behavior. As a result of not able to do experiments at laboratory, the assumptions for column leaching data were considered, but the outputs did not match the fundamentals and scientific backgrounds. So, the results of heap leaching test were provided by literatures. The results were assumed to able to present heap leaching behaviors under alkaline glycine solution and diluted sulfuric acid.

4.2 Characterization of low-grade copper ore.

The chemical and phase analyses were supposed to be carried out in laboratory to identify the initial head assays and mineralogical phase in low-grade copper ore. However, it would not be able to do laboratory, general data of mineralogical phases and copper content data were provided from “Achit-ikht” LLC shown **Table-15**.

Considering the pure copper grade in the ore is around 0.316 %. Chalcocite, covellite, chalcopyrite, bornite, cuprite and copper bearing minerals like copper carbonates and sulfides are dominated in the ore. The **table-15** shows the compositions of the copper bearing minerals and content of pure copper exists in entire 2nd dump of EMC.

Due to lack of data for leaching experiments and absence of own laboratory data, composition of mineral phase of ore assumptions were considered. The assumption 1 includes: in the low-grade copper ore 3 kinds of mineral phase were resided such as chalcocite, chalcopyrite and cuprite. The assumption 2 includes: due to lack of data for leachability of copper minerals that exists in the ore like covellite, bornite and copper carbonates and other sulfide minerals in the literatures. Leaching behaviors of the chalcocite - covellite, chalcopyrite – bornite – copper carbonates and sulfides were assumed to have same characteristics. These two assumptions were used in an important role for performing further bottle roll experiments and tests.

Table 15 / Copper mineral phases in 2nd dump of EMC/

Name of minerals and phase composition	Content %		Weight of Copper in dump [ton]
	Mineral phase % in dump	Pure copper % in dump	
Chalcocite /Cu2S/	0.16 %	0.124	69477 tons
Covellite /CuS/	0.07 %	0.048	26842 tons
Chalcopyrite /CuFeS2/	0.21 %	0.073	40717 tons
Bornite /Cu5FeS4/	0.03 %	0.014	7896 tons
Cuprite /Cu2O/	0.08 %	0.008	4603 tons
Copper Carbonates and Sulfides /CuCO3, CuS, Cu2S /	0.07 %	0.049	22465 tons
Silica /SiO2/	66.14 %		-
Aluminum oxide /Al2O3/	15.85 %		-
Hematite /Fe2O3/	4.95 %		-

4.2.1 Particle size distribution

The dry sieve analysis was performed for column leaching tests. The eight samples from proposed ores of each columns were sieved to study uniform distribution of particle sizes. To explain the distribution of particle sizes, two 2 kinds of graphs is used such as Gaudin-Schumann and Rosin-Rammler. In the experiment the Rosin-Rammler distribution graph was used to show the distributions. **Graphs-15** shows how particle sizes were distributed uniformly in eight samples from column leaching experiments.

/Appendix-1/

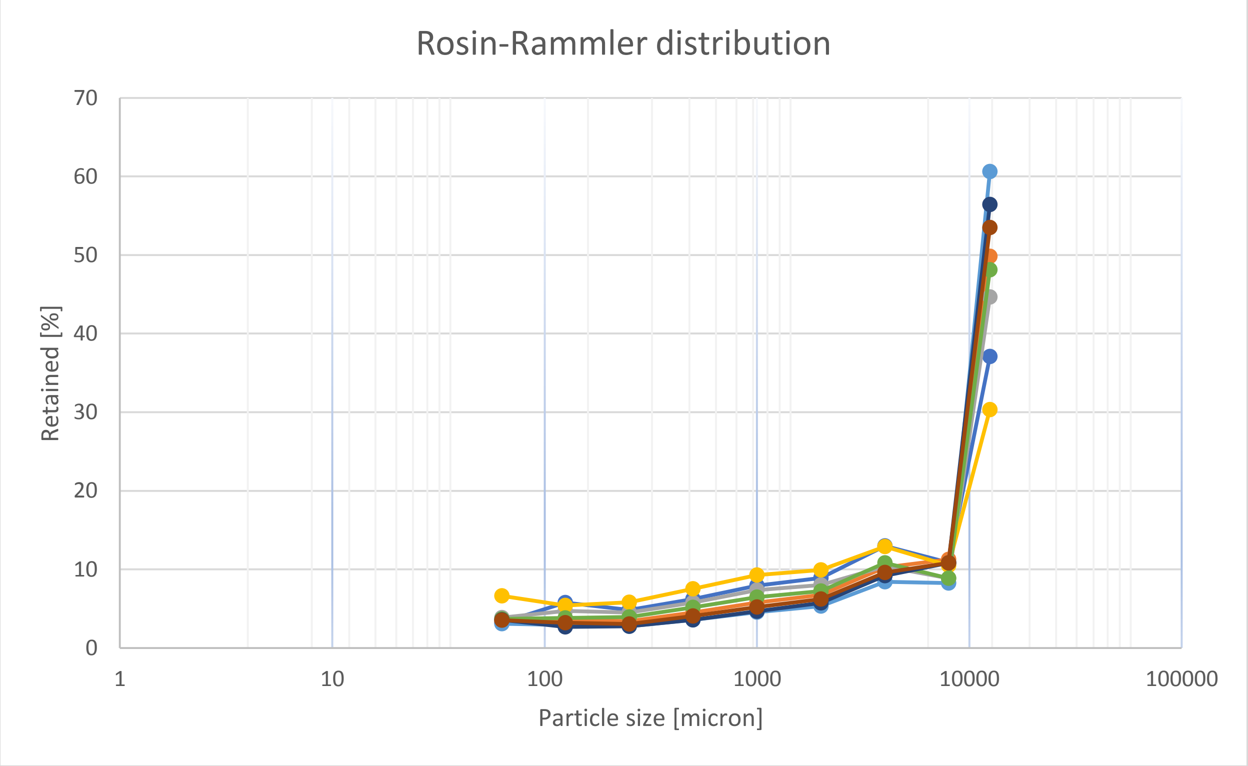


Figure 15 /Rosin-Rammler distribution from 8 samples from column leaching tests/

4.3 Results of Leaching behavior of low-grade copper ore.

4.3.1 Effect of initial glycine concentrations of low-grade copper ore /Test-1/

The effect of glycine concentration tests was carried out for low-grade copper ore with the initial pH of leach solution was kept constant at 11 during glycine concentration were varied based on a glycine to copper molar ratio. The reason for the using molar ratio of glycine and copper to prepare the leach solution was the glycine forms stable complex with copper under specific pH values between 4 and 12. For example in order to form $Cu(H_2NCH_2COO)_2$ complex 2 moles of glycine is needed for 1 mole copper. The ratios of Glycine : Copper obtained were 2:1, 4:1, 8:1 respectively. Each test was performed 3 times due to lower the errors. Due to primary and secondary copper ore composition domination, to oxidize these ores, 0.5% hydrogen peroxide in leach solution was used in further tests. The effect of glycine concentration on the copper metal recovery is shown the **figure-16.** The graph shows copper recovery increases while the concentration of leaching solution glycine increases. Metal recoveries used in the graph was the average values from 3 tests results. /Result of metal recoveries are assumed and calculated on the **Appendix**/ Considering the economical side and near metal recovery, further investigations were carried out under glycine solution as a Gly:Cu=4:1 ratio of concentration. /The copper concentration at given states were calculated and assumed on the **Appendix** /.

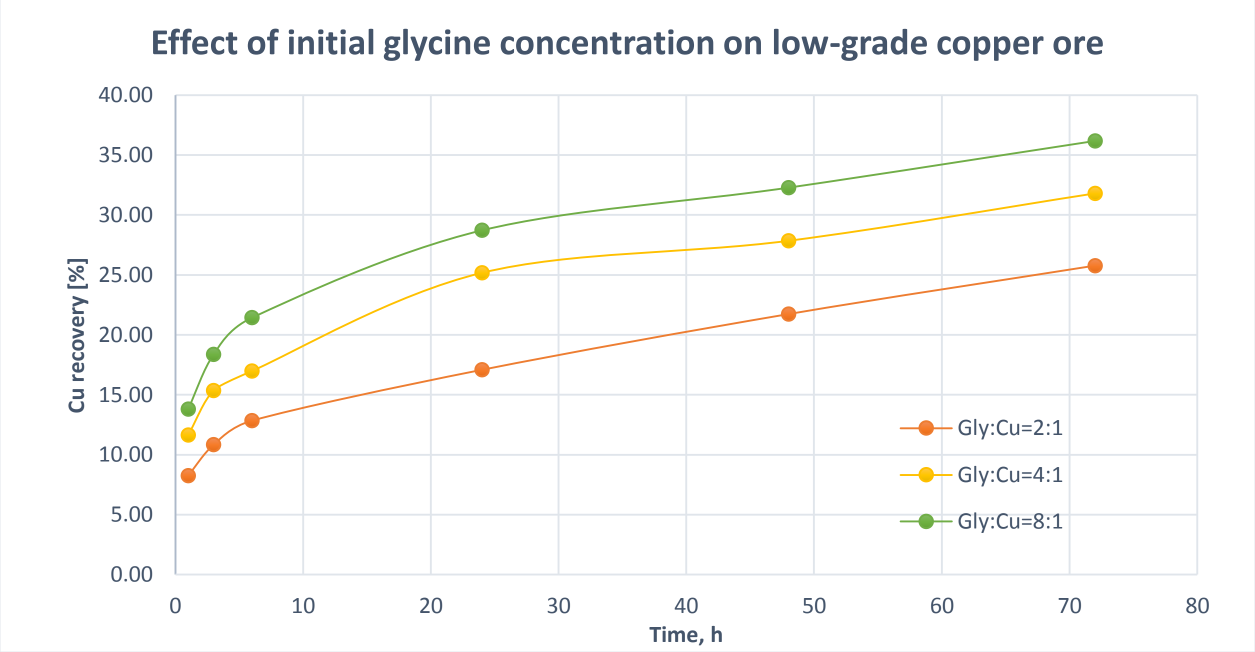
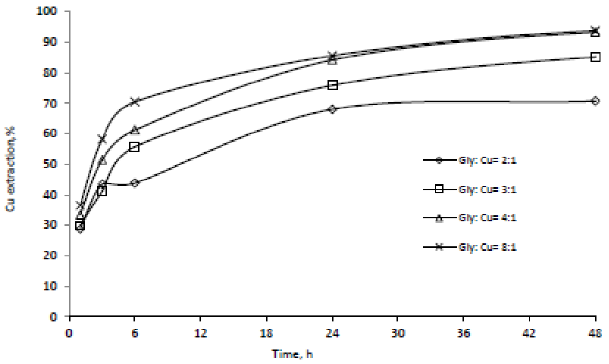


Figure 16 /Effect of initial concentration tests on the leaching of low-grade copper ore/

Assumptions were used to calculate the further metal recovery results. The results of metal recoveries of copper specimens were reported as metal extraction graphs and appendixes on the (Tanda, 2017). The ore was assumed that it consists of three copper minerals phase including cuprite, chalcopyrite and chalcocite. So, the data of these copper minerals used for the calculating metal recovery of low-grade copper ore that contains 0.316 % pure copper. Based on the mineral compositions in damp data from **Table-15,** each copper minerals would contain the reported amount of copper weight. Also, each copper minerals have different metal extraction rate. So**,** the assumption rises that the fixed amount of copper weight is extracted over time with rate of its original copper mineral phase. Then combination of each metal recovery creates low-grade copper ore's metal extraction curve.

For example, the **figures**-**17,18 and 19** show that cuprite, chalcopyrite and chalcocite metal recovery curves respectively. The combined metal extraction curve is more similar to chalcocite's metal recovery curve.



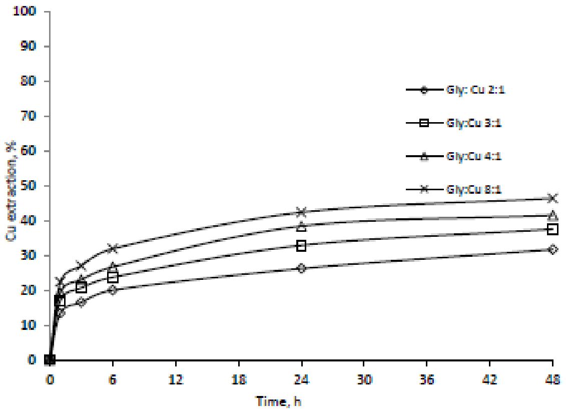


Figure 17 /Metal recovery curve of Cuprite at various concentrations/

Figure 18 / Metal recovery of Chalcocite at various C/

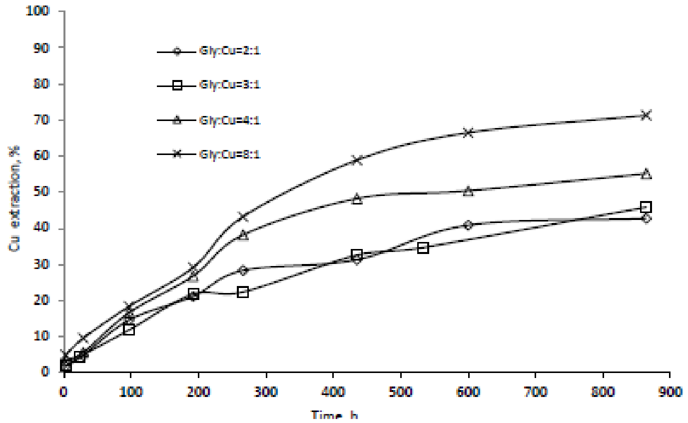


Figure 19 / Meatal recovery of Chalcopyrite at different C of glycine/

4.3.2 Effect of initial pH values on dissolution of low-grade copper ore. /Test-2/

To get understand of low-grade copper ore leaching behavior in alkaline glycine solution at various initial pH values and leach duration, initial concentration of glycine solution was kept constant at molar ratio of Glycine : Copper = 4 : 1 respectively, leach solutions were prepared at 9, 10 and 11 pH values and 0.5 % hydrogen peroxide was added. During the test, pH values were uncontrolled from observation. For example, the solution at initial pH value of 11 was investigated in tests, afterwards pH value dropped into 9.8 at the end of test (Chemuta, 2017). From **figure-17**, leaching at pH value of 9 and pH value of 10 had higher copper extraction at the beginning. But the time goes, leaching at pH value of 9 decreases over time and stabilized. (Chemuta, 2017) noted that it can actually be seen that dissolved copper at pH 10 started to decrease as this was associated to a light blue precipitate formation. (Gylienee, 2001) had reported about the precipitation of $Cu(Gly)_2$, *When investigating the removal of heavy metals in solutions by complexing them with glycine and EDTA. The metal complex was then reported to precipitate after several hours or days.* Thus, the temperature, pH and copper concentration influence the dissolution of copper ores in alkaline glycine to form Copper-Glycine complexes. To comment that the maximum average dissolution of copper results at pH value of 11, pH value of 10 and pH value of 9 with 0.5 % hydrogen peroxide are 1.27 g / L, 1.14 g / L and 0.99 g / L respectively. **/on Appendix/**

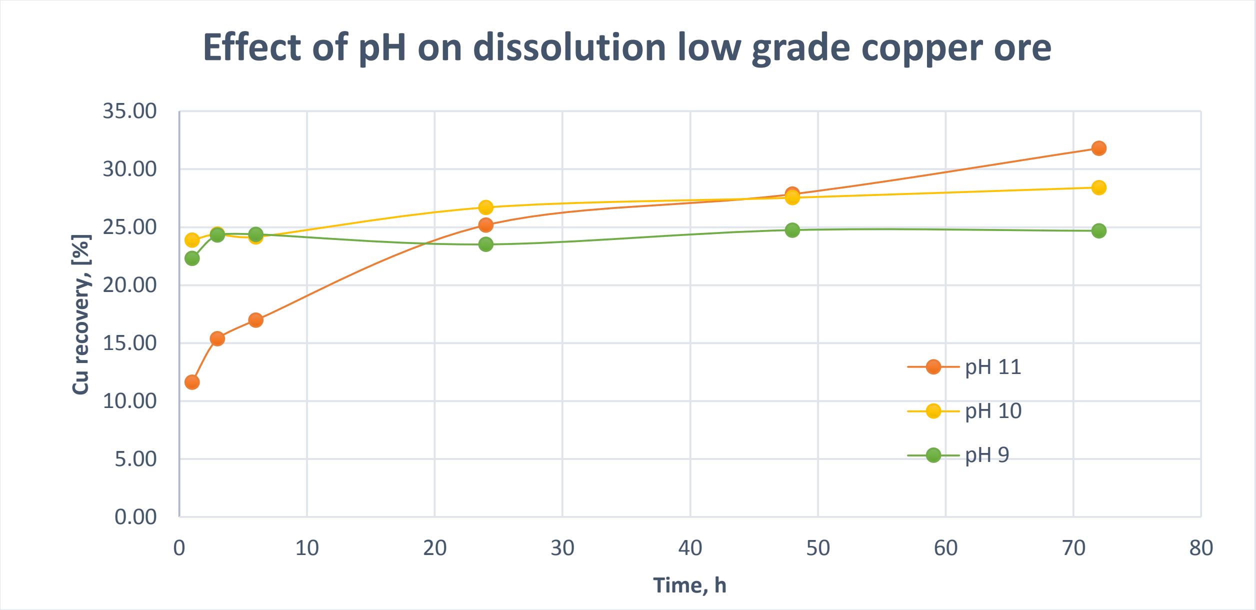


Figure 20 / Effect of initial pH values tests on the leaching of low-grade copper ore/

4.3.3 Effect of hydrogen peroxide in dissolution of low-grade copper ore /Test-3/

The hydrogen peroxide, chemical formula of H_2O_2, was investigated as oxidizing agent for minerals with low dissolution rate including primary and secondary types of copper ores /Chalcocite, Chalcopyrite and copper carbonates/. Effect of hydrogen peroxide in dissolution of low-grade copper ore tests were carried out at constant initial concentration of glycine molar ratio of Glycine : Copper = 4 : 1 respectively and under constant pH value of 11 while 0 %, 0.5 %, 1 % of volume hydrogen peroxide in 500 ml leach solution were utilized. The graph shows that beginning of metal recoveries are different but when the time goes, metal recoveries get closer to each other. The metal recovery of leaching test at absence of hydrogen peroxide was slow at the beginning and it rises constantly over time. At the beginning, for an hour, leaching test absence of hydrogen peroxide had 5.34 % of metal recovery. For three hours of leaching, it showed 10.59 % of metal recovery. With 0.5 % and 1 % hydrogen peroxide leaching tests showed 11.64 %, 15.37 % and 12.99 %, 17.00 % metal recoveries for first hour and for three hours of leaching respectively. From these results, it can be said that hydrogen peroxide can influence on dissolution rate to modify the reaction at the beginning of leaching period. And also, it can be reported that hydrogen peroxide being used up or decomposed within first few hours of leaching.

The results can be concluded that hydrogen peroxide is possible to applied for increasing dissolution rate of low-grade copper ore. **/Appendix/**

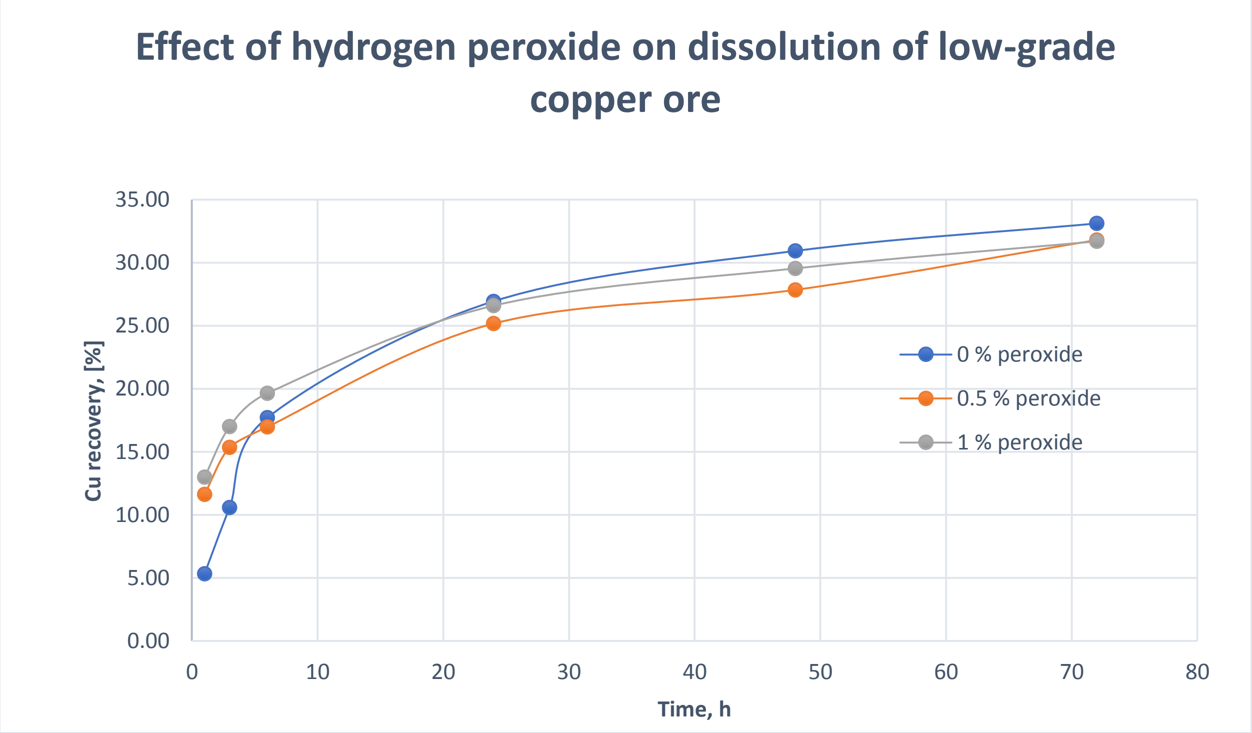


Figure 21 / Effect of initial hydrogen peroxide content tests on the leaching of low-grade copper ore/

4.3.4 Comparison test between alkaline glycine and diluted sulfuric acid leaching /Test-4/

The leaching behavior test in bottle roll were carried out in different leach solutions like alkaline glycine solution and diluted sulfuric acid. The alkaline glycine based test was performed under constant initial concentration of glycine and copper molar ratio of 2 : 1 proportionally, pH value of 11 and with 0.5 % of hydrogen peroxide in leach solution. And the conventional sulfuric acid-based test was performed under constant initial concentration of sulfuric acid and copper molar ratio of 2 : 1 respectively and with 0.5 % of peroxide. The graph shows that how metal recoveries difference between alkaline glycine based and conventional sulfuric acid-based leaching. For sulfuric acid concentration was quite high comparing to sulfuric acid concentration used in heap operations. Also, it shows great amount of metal recoveries, about 3 times greater than alkaline glycine-based leaching. For instance: after 72 hours of leaching, glycine-based system had 25.78

% of copper extraction and sulfuric acid-based system had 61.82 %. The assumed and calculated data for the comparison tests provided on /**Appendix/.**

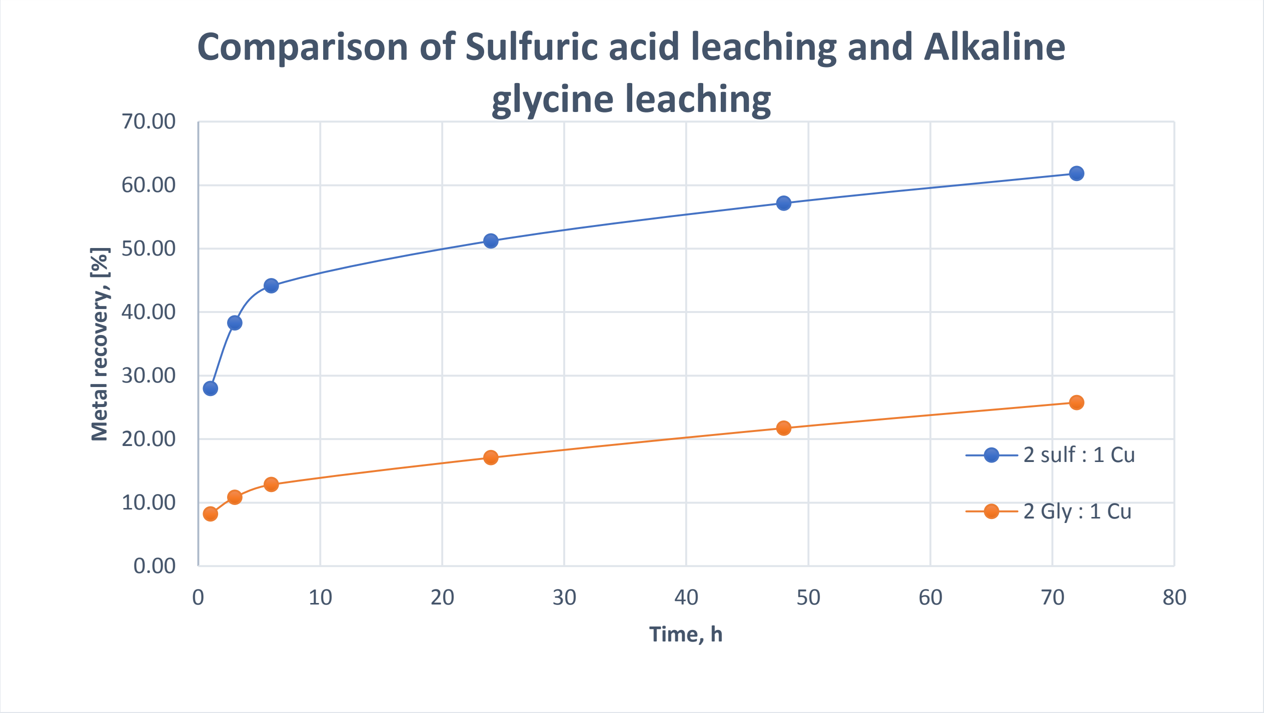


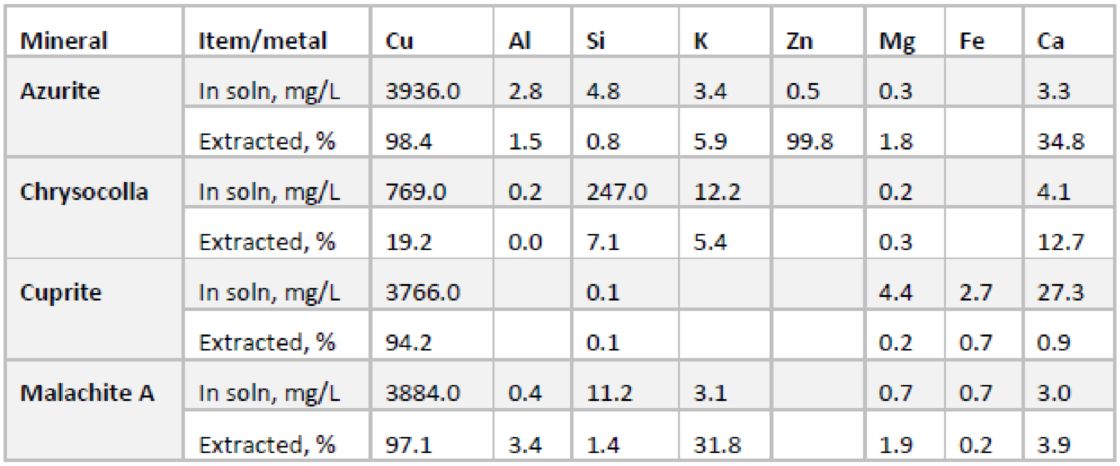
Figure 22 / Comparison test of glycine leaching behavior with sulfuric acid leaching behavior on low-grade copper ore/

4.3.5 Dissolution of impurities

The conventional leaching agent sulfuric acid for dissolution of copper oxides tend to react with a wide range of impurities (iron, silicon, magnesium, calcium, aluminum, etc.). The formation of complex with impurities might form precipitate and contaminate the leaching solution that causes negatively influence solvent extraction and electrowinning processes. (Tanda, 2017) showed that analyses for determination of impurity elements in final alkaline glycine leach solutions from copper mineral specimens leaching tests like copper oxides, chalcopyrite leaching tests by using ICP. For example, in final leach solution from chrysocolla leaching test, *247 mg / L* Si was detected in the leach solution. But it only represents *7 % of total Si in the sample*. From the other side, if sulfuric acid was used as leach solution, *3456 mg / L of Si would be presented in the leach solution*. And also, (Tanda, 2017) reported *that arsenic and lead are observed to dissolve more at pH 9 and 10. Zinc leaching follows the same trend as that of copper with higher extraction noted as the pH increased. A zinc extraction of 60.0 % occurred at pH 11 while only 20.0 % zinc* *was obtained at pH 9. Under all conditions, less than 1.0 % Si and Mg were leached. Except for when pH is 9, less than 6 % Fe was leached under the other used conditions.*

At the end, it can be noted that alkaline glycine solution with pH above 11 productively leach copper minerals while rejecting most gangue minerals and metals in the pregnant leach solution. In other hand, above pH 11 glycine solution do not form complexes with most impurity metals like Fe and glycine consumption is lower than sulfuric acid consumption on oxide copper minerals which is proved. It means that if the alkaline glycine system applied in heap leaching technique, alkaline glycine solution will be recycled under less cost than sulfuric acid due to leach solution consumption.

Table 16 / Concentration of copper and impurities in the final leach solutions and the calculated degree of extraction from leaching copper oxides: Gly:Cu 4:1, pH 11, P_{100} 75 micron/



Mineral	Item/metal	Cu	Al	Si	K	Zn	Mg	Fe	Ca
Azurite	In soln, mg/L	3936.0	2.8	4.8	3.4	0.5	0.3		3.3
	Extracted, %	98.4	1.5	0.8	5.9	99.8	1.8		34.8
Chrysocolla	In soln, mg/L	769.0	0.2	247.0	12.2		0.2		4.1
	Extracted, %	19.2	0.0	7.1	5.4		0.3		12.7
Cuprite	In soln, mg/L	3766.0		0.1			4.4	2.7	27.3
	Extracted, %	94.2		0.1			0.2	0.7	0.9
Malachite A	In soln, mg/L	3884.0	0.4	11.2	3.1		0.7	0.7	3.0
	Extracted, %	97.1	3.4	1.4	31.8		1.9	0.2	3.9

4.3.6 Discussion of leaching behavior of low-grade copper ore

However, results came from the assumptions, it can represent the leaching behavior of low-grade ore in alkaline glycine and sulfuric acid. The dissolution behavior of low-grade copper ore which contains 0.316 % of copper and three phases of copper mineral have been investigated at different Gly : Cu molar ratios, initial solution pH, and peroxide concentration. The observation from the experiments was that higher Gly-Cu ratios favor copper dissolution in low-grade copper ore. Initial solution pH of 11.0 was reported to be the optimum for the dissolution of the cut-off grade ore.

Lower than 9.5 pH leaching solution causes precipitation of copper-glycine complex in the alkaline glycine solution. Leaching at 9 or 10 pH in alkaline glycine solution, the metal recovery showed unstable results on the low-grade copper ore. At beginning of leaching time, it dramatically increased then it dropped. The drop of the graph was noted on the (Tanda, 2017) the precipitation was formed. Then the graph rises again means that copper precipitations leached again to increase the metal recovery.

Hydrogen peroxide that was investigated as strong oxidant but it did not influence on metal recovery significantly. It can be said that peroxide influenced to metal extraction rate at the beginning of leach time and it runs out.

Comparing alkaline glycine leaching system with sulfuric acid leaching system. For the best comparison, the comparison test was carried out almost same as 2:1 gly : Cu test of Test-1. But it showed nearly sulfuric acid leaching has 3 to 4 times greater than alkaline glycine leaching system.

All in all, dissolution of impurities in alkaline glycine analyses were carried out on the (Tanda, 2017). The research result said that 247 mg / L silica was detected at the alkaline glycine solution. If the leach solution were the diluted sulfuric acid it would be noted that 3456 mg / L silica would be detected. From this result, it would be concluded that glycine solution would react much as sulfuric acid with gangue minerals and acid consuming minerals like carbonates and silicates. In other hand, If the alkaline glycine solution is used for the heap leach application which contains high impurities, the new system would be succeed.

4.4 Heap leaching behavior on low-grade copper ore.

The most economical method for processing low-grade copper ore containing gangue minerals, is the heap and dump leaching techniques. Due to unable to do experiments on laboratory, all procedures and methods of heap leaching behavior in different leach solution were supposed to be performed according to the procedure outline in the **section 3.4.3.** The assumptions of heap leaching behavior tests results were considered to calculated from other closest data. But It did not succeed. So, further study would continue on results of heap leaching tests from the literatures to compare heap leaching behavior in alkaline glycine solution and diluted sulfuric acid.

4.4.1 Heap leaching behavior results from literatures

Based on 2 literatures (Tanda, 2017), (Sukhbaatar.B, 2019), heap leaching behavior of alkaline leaching solution on low-grade copper and heap leaching behavior of diluted sulfuric acid leaching solution on low grade copper were studied.

(Tanda, 2017) carried out the column leaching tests on 5 kg Cu-Au ore with circulation of leach solution. Mineralogy of investigated ore is a low-grade chalcopyrite containing gold. The experiment was performed in 2 columns with different concentrations (0.1 M and 0.5 M) of alkaline glycine solution, at constant initial pH value of 11 and with constant flow rate of 33 L / m2 / h. The dissolution of copper was noted that 6 % of copper extracted after 36 days for 0.5 M and 3.5 % with 0.1 M glycine. Even though, copper dissolution rate is slow, the steady increase over time as shown in **figure-23**. For the gold dissolution, 1.61 % of metal recovery was noted after 159 days.

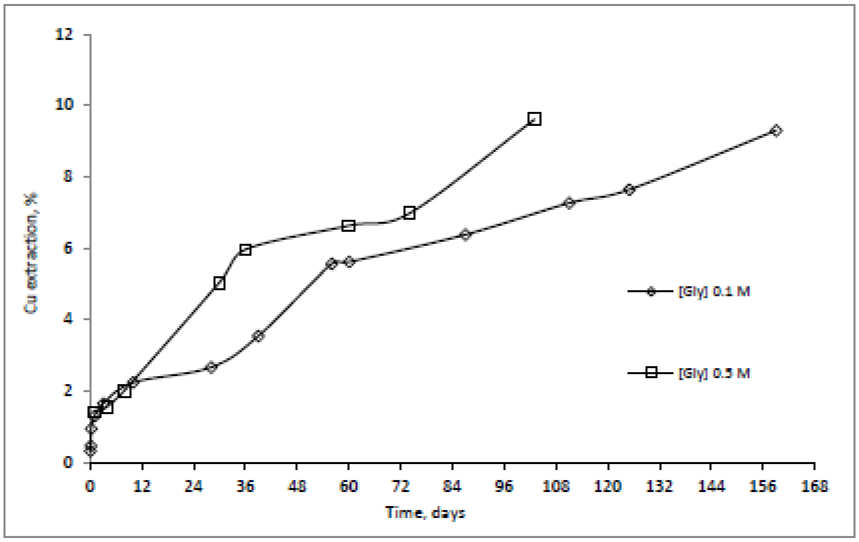
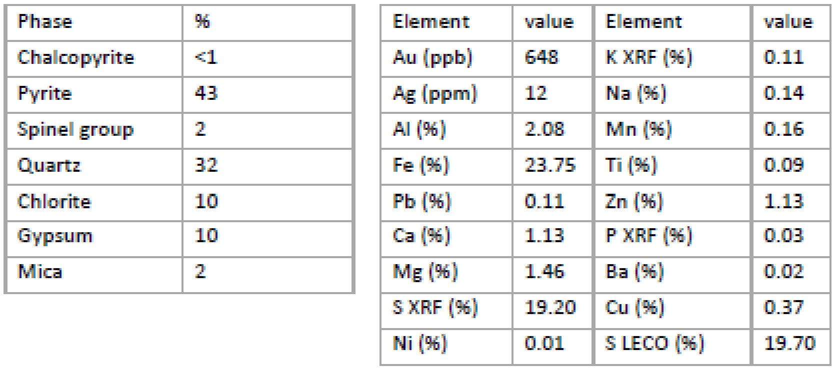


Figure 23 / Column Cu leaching from Cu-Au ore (low-grade gold containing chalcopyrite ore), pH 11, 33 L/ m2/ h. /

From this graph, it can be reported that leaching rate depends on the mineral grains. In other word, it is dependent on the copper minerals locations in ore body. For example, in the graph, first 12 days the copper extraction increased exponentially. Then between 12 to 36 days extraction rate increased constantly. And increasing dramatically again. It means, firstly within 12 days, the leaching reaction occurs at surface of the particle. Then between 12 to 36 days, leach solution exposed to copper mineral that locates at middle by pores or crack of particles. Starting from 36 days, the leaching reaction occurs at middle of ore body.

(Tanda, 2017) also performed other column leaching test on a flotation tail from copper processing plant in Western Australia. Mineralogical analysis of the proposed ore said that the only one copper mineral phase was chalcopyrite. XRF analysis showed that flotation tail contains 0.37 % copper. The copper content of flotation tail is same as low-grade copper ore of 2nd dump of EMC from "Achit-Ikht" LLC. The **table-18** shows Mineralogy and elemental composition of Cu-Au flotation tail from copper processing plant.

Table 17 / Mineralogy and elemental composition of Cu-Au ore (tail of flotation) /



Phase	%
Chalcopyrite	<1
Pyrite	43
Spinel group	2
Quartz	32
Chlorite	10
Gypsum	10
Mica	2

Element	value	Element	value
Au (ppb)	648	K XRF (%)	0.11
Ag (ppm)	12	Na (%)	0.14
Al (%)	2.08	Mn (%)	0.16
Fe (%)	23.75	Ti (%)	0.09
Pb (%)	0.11	Zn (%)	1.13
Ca (%)	1.13	P XRF (%)	0.03
Mg (%)	1.46	Ba (%)	0.02
S XRF (%)	19.20	Cu (%)	0.37
Ni (%)	0.01	S LECO (%)	19.70

The column /d = 90 mm/ leaching test was performed at ambient temperature and atmospheric pressure. The leaching solution at pH value of 11 containing of 0.5 M was circulated at a rate of 135 L / m2 / h (0.86 L / h). After 48 days of leaching, result came out with 53.6 % metal recovery of copper. The dissolution of gold was reported that 7.6 % of metal recovery after 48 days. The **figure-21** shows that copper metal recovery over time containing 0.5 M alkaline glycine solution.

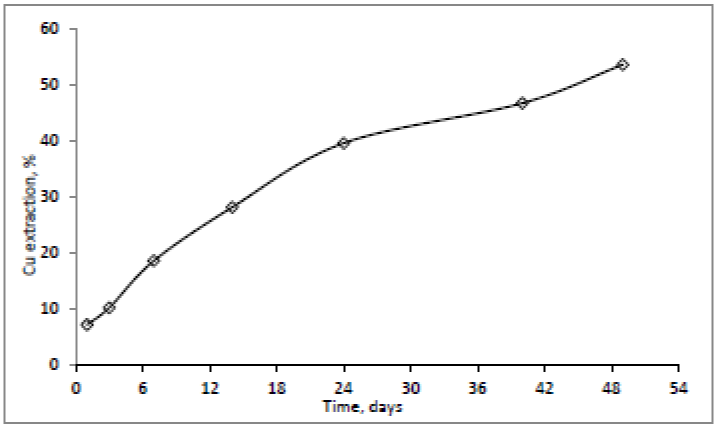


Figure 24 /Column Cu leaching from Cu-Au ore (tail of flotation) pH 11, 0.839 L/ h, /

(J.J.Eksteen, 2017) has reported that glycine only (without catalyst) leaching shows slow leach rate. At elevated temperature the leach rate would increase on both Cu and Au leaching by alkaline glycine solution. The leach rates, even at elevated temperature remain far too slow for agitated tank leach systems, but it is considered to have potential for heap leach or in situ leach systems.

(Sukhbaatar.B, 2019) performed column leaching tests for optimizing the flow rate of leach solution for 15 days. In the experiment, constant initial concentration of 3 g / L sulfuric acid was utilized with various flow rates on low-grade copper ore of 2nd dump from “Achit-Ikht” LLC. The three columns were investigated, each column (d=240mm) leaching tests has different flow rates. For example, column-1 has 5.46 L / h/ m2 (0.906 L / h), 16.4 L / h/ m2 (2.724 L / h) for column-2 and 10.25 L / h/ m2 (1.702 L / h) for column-3 flow rates. The **graph-22** shows the copper metal extractions depending on flow rate of leaching solution over time. The test with the highest flow rate reached the highest metal recovery. After 15 days, the test with highest flow rate had 40 % of metal recovery. The test with the lowest flow rate had 28 % metal recovery after 15 days.

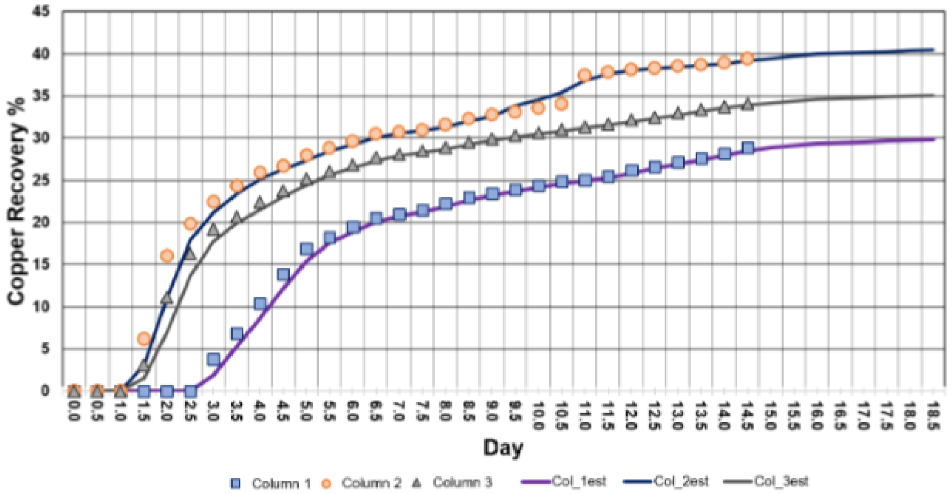


Figure 25 /Column Cu leaching from low-grade copper ore under 3 g/L sulfuric acid, 0.906 L/ h (Sukhbaatar.B, 2019)/

4.4.2 Discussion of heap leaching behavior of low-grade copper ore.

First experiment was performed under different concentration including 0.1 M and 0.5 M of glycine was investigated. It showed the slow copper extraction rate 10 % of copper was extracted after 108 hours with 0.1 M glycine, around 10 % of copper was extracted after 168 hours of leaching time. The ore was investigated in this test was low gold containing chalcopyrite with high content of impurities.

Second experiment was performed on tail flotation tail process under 0.5 M alkaline glycine at pH 11. The ore was analyzed by XRF. 0.37 % copper contains in the flotation tail. 53.6 % copper recovery was observed. From these 2 results, ore type, mineralogy, grain size and content of head assays are the main factor that influences to metal extraction of ore body in glycine leach solution.

Third experiment was performed on low-grade ore from Erdenetiin-Ovoo in Mongolia under concentration of 3 g / L diluted sulfuric acid. Only after 15 days, with highest flow rate test reached 40 % of metal recovery. The lowest flow rate of this study was similar to the second experiment with 0.5 M alkaline glycine solution on flotation tail. Comparing to each result, sulfuric acid has about 2 times greater metal recovery.

5. Conclusion

The low-grade copper ore of 2nd damp EMC than contains 0.316 % copper and mineral phases including 0.16 % of chalcocite, 0.07 % of covellite, 0.21 % of Chalcopyrite, 0.03 % Bornite and 0.08 % of cuprite and other copper bearing minerals like copper carbonates. Due to unable to do laboratory work, the metal recovery curve was assumed from individual metal extraction of copper mineral specimens.

Investigations into the leaching behavior of low-grade copper ore in alkaline glycine solutions, in order to evaluate the extent of copper dissolution form common copper minerals, were conducted using a bottle roller at different glycine concentrations and at different initial leach solution pH values. The most favorable conditions, for leaching low-grade copper ore in alkaline glycine solution, are 4:1= glycine : copper, pH values of 11 and 0.5 % peroxide. The result of this condition was 31.8 % of copper extraction after 72 hours of leaching time.

The main aim of this bachelor thesis work is to achieve the following objectives:

- To investigate and establish the leaching behavior of low-grade copper minerals in the alkaline glycine solutions by using bottle roll tests (yes it has been done, but the all results was assumed)
- To study the effects of process variables and impurities in the dissolution of copper from copper ores under glycine solution. /various initial concentration of reagent, hydrogen peroxide and pH (The effects of process variables were determined with help of literatures)
- To investigate and establish the heap leaching behavior of low-grade copper minerals in the alkaline glycine solutions by using column leaching test. (Although it did not be assumed, but same proposed scientific paper was provided to explain the heap leaching behavior)
- To study the effects of glycine leach solution concentration and flow rate of leach solutions in column leaching tests. (Same as above)

The main significant outcomes would be:

- To introduce an environmentally benign process for treating various types of copper ores. (Reported on MSDS)
- To enable treatment of ores which fall below cut-off grades for conventional processes. (In the literatures it is possible to applied on the heap leaching technique. But the research did not provide the optimal operating parameters, it showed the leaching behavior of low-grade copper ore.)
- To compare new reagent glycine with conventional reagent sulfuric acid by dissolution rate and dissolved impurities. (From observation of alkaline glycine has medium reagent cost, environmentally friendly, slow dissolution rate and selectively leach the valuable minerals. On the other hand, sulfuric acid has low reagent cost, environmentally harmful, relatively high dissolution rates on oxidized copper ore, not selectively leach valuable minerals and it has high chance to react with other gangue minerals)

At starting of the bachelor work the hypothesis was noted that:

- By increasing its glycine leach solution concentration, metal recovery would increase over time (agreed and matched)
- With higher content of hydrogen peroxide as oxidant tests would have more dissolution rate (it was noted that hydrogen peroxide can modify the dissolution rate at beginning of leaching time)
- Low amount of impurities would dissolve in the glycine leach solution (agreed and matched on the literature)
- Alkaline glycine has lower dissolution rate than diluted sulfuric acid on the low-grade copper ore (Agreed and matched)
- The test with higher concentration of leach solution will have higher metal recovery (matched and agreed)
- Heap leaching dissolution rate would be lower than bottle roll leaching dissolution rate (absolutely agreed)
- Glycine-based heap leaching test has lower metal recovery than sulfuric acid-based heap leaching test (agreed)

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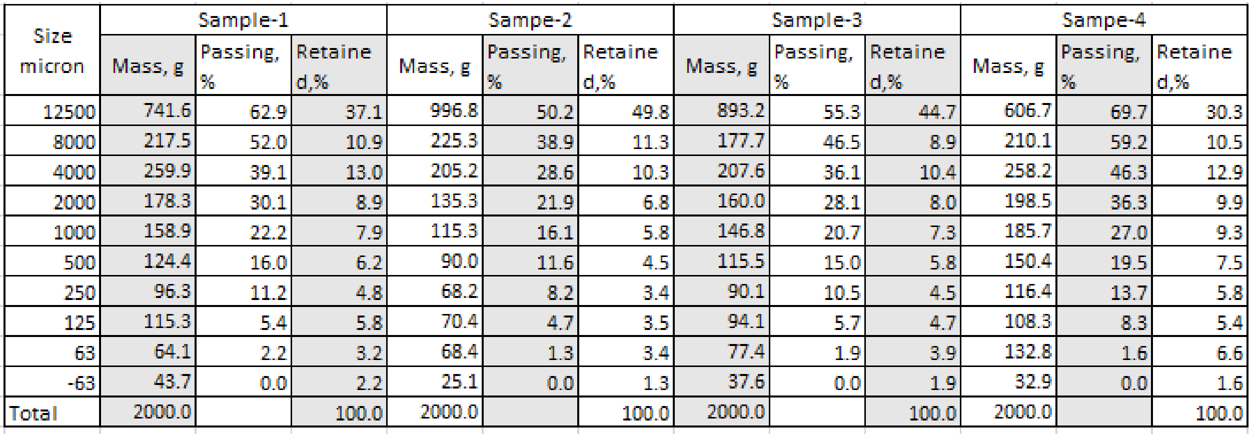
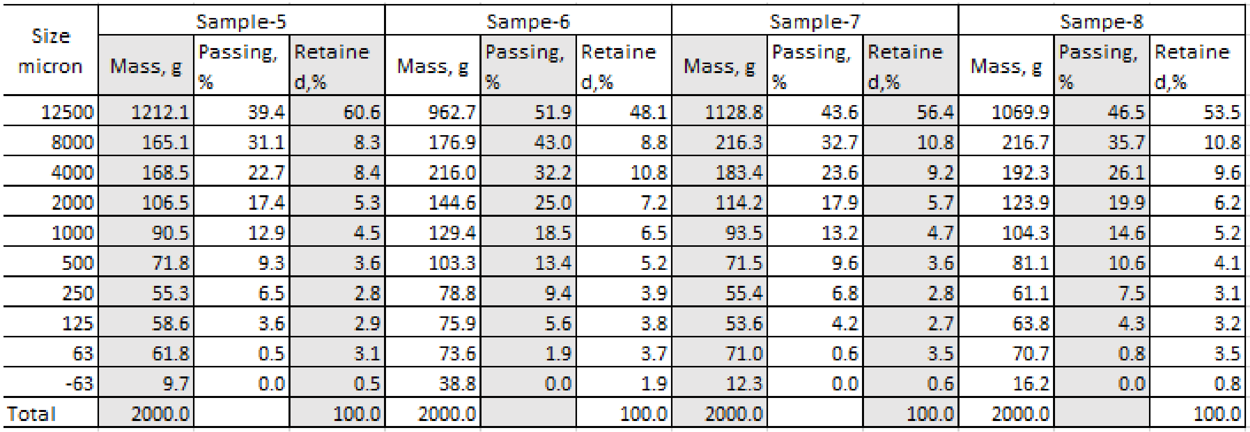
7. Appendices

Table 18 /Sieve analysis data for 4 columns/



Size micron	Sample-1			Sampe-2			Sample-3			Sampe-4		
	Mass, g	Passing, %	Retained,%	Mass, g	Passing, %	Retained,%	Mass, g	Passing, %	Retained,%	Mass, g	Passing, %	Retained,%
12500	741.6	62.9	37.1	996.8	50.2	49.8	893.2	55.3	44.7	606.7	69.7	30.3
8000	217.5	52.0	10.9	225.3	38.9	11.3	177.7	46.5	8.9	210.1	59.2	10.5
4000	259.9	39.1	13.0	205.2	28.6	10.3	207.6	36.1	10.4	258.2	46.3	12.9
2000	178.3	30.1	8.9	135.3	21.9	6.8	160.0	28.1	8.0	198.5	36.3	9.9
1000	158.9	22.2	7.9	115.3	16.1	5.8	146.8	20.7	7.3	185.7	27.0	9.3
500	124.4	16.0	6.2	90.0	11.6	4.5	115.5	15.0	5.8	150.4	19.5	7.5
250	96.3	11.2	4.8	68.2	8.2	3.4	90.1	10.5	4.5	116.4	13.7	5.8
125	115.3	5.4	5.8	70.4	4.7	3.5	94.1	5.7	4.7	108.3	8.3	5.4
63	64.1	2.2	3.2	68.4	1.3	3.4	77.4	1.9	3.9	132.8	1.6	6.6
-63	43.7	0.0	2.2	25.1	0.0	1.3	37.6	0.0	1.9	32.9	0.0	1.6
Total	2000.0		100.0	2000.0		100.0	2000.0		100.0	2000.0		100.0

Table 19 /5-8 column sieve analysis/



Size micron	Sample-5			Sampe-6			Sample-7			Sampe-8		
	Mass, g	Passing, %	Retained,%	Mass, g	Passing, %	Retained,%	Mass, g	Passing, %	Retained,%	Mass, g	Passing, %	Retained,%
12500	1212.1	39.4	60.6	962.7	51.9	48.1	1128.8	43.6	56.4	1069.9	46.5	53.5
8000	165.1	31.1	8.3	176.9	43.0	8.8	216.3	32.7	10.8	216.7	35.7	10.8
4000	168.5	22.7	8.4	216.0	32.2	10.8	183.4	23.6	9.2	192.3	26.1	9.6
2000	106.5	17.4	5.3	144.6	25.0	7.2	114.2	17.9	5.7	123.9	19.9	6.2
1000	90.5	12.9	4.5	129.4	18.5	6.5	93.5	13.2	4.7	104.3	14.6	5.2
500	71.8	9.3	3.6	103.3	13.4	5.2	71.5	9.6	3.6	81.1	10.6	4.1
250	55.3	6.5	2.8	78.8	9.4	3.9	55.4	6.8	2.8	61.1	7.5	3.1
125	58.6	3.6	2.9	75.9	5.6	3.8	53.6	4.2	2.7	63.8	4.3	3.2
63	61.8	0.5	3.1	73.6	1.9	3.7	71.0	0.6	3.5	70.7	0.8	3.5
-63	9.7	0.0	0.5	38.8	0.0	1.9	12.3	0.0	0.6	16.2	0.0	0.8
Total	2000.0		100.0	2000.0		100.0	2000.0		100.0	2000.0		100.0

Table 20 /2gly : 1Cu vs time 0.5% peroxide, at pH 11/

Leaching Conditions	Time , hrs	[Cu] , g/L	% Cu extraction	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	Ave [Cu], g/L	Ave % Cu extraction
2 Gly : 1 Cu Sample=2g Cu DI=500ml, Initial pH=11, Peroxide=8.3 3 ml 0.5%	1	0.32	8.08	0.15	7.54	0.18	9.15	0.22	8.26
	3	0.43	10.82	0.21	10.54	0.22	11.14	0.29	10.83
	6	0.52	13.09	0.25	12.40	0.26	13.05	0.34	12.85
	24	0.70	17.56	0.35	17.60	0.32	16.10	0.46	17.09
	48	0.89	22.16	0.43	21.45	0.43	21.60	0.58	21.74
	72	1.02	25.50	0.52	26.14	0.51	25.69	0.69	25.78

Table 21 / 4 Gly : 1 Cu pH = 11 pH 0.5 % /

Leaching Conditions	Time, hrs	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	Ave [Cu], g/L	Ave % Cu extraction
4 Gly : 1 Cu Sample=2g Cu DI=500ml, Initial pH=11, Peroxide=8.3 3 ml 0.5%	1	0.47	11.84	0.44	10.97	0.48	12.10	0.47	11.64
	3	0.61	15.25	0.59	14.65	0.65	16.20	0.61	15.37
	6	0.70	17.62	0.65	16.14	0.69	17.21	0.68	16.99
	24	1.01	25.25	0.99	24.68	1.02	25.60	1.01	25.18
	48	1.14	28.51	1.09	27.14	1.12	27.90	1.11	27.85
	72	1.27	31.67	1.27	31.64	1.28	32.10	1.27	31.80

Table 22 /8 Gly : 1 Cu, initial pH -11, with 0.5 %/

Leaching Conditions	Time, hrs	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	Ave [Cu], g/L	Ave % Cu extraction
8 Gly : 1 Cu Sample=2g Cu DI=500ml, Initial pH=11, Peroxide=8.3 3 ml 0.5%	1.00	0.55	13.81	0.54	13.50	0.56	14.10	0.55	13.80
	3.00	0.73	18.28	0.73	18.14	0.75	18.69	0.73	18.37
	6.00	0.86	21.48	0.87	21.69	0.85	21.13	0.86	21.43
	24.00	1.16	28.95	1.12	27.97	1.17	29.24	1.15	28.72
	48.00	1.31	32.80	1.25	31.14	1.32	32.90	1.29	32.28
	72.00	1.45	36.26	1.41	35.15	1.49	37.13	1.45	36.18

Table 23 /4 gly : 1 Cu, initial pH=9 0.5 % hydrogen peroxide/

Leaching Conditions	Time, hrs	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	Ave [Cu], g/L	Ave % Cu extraction
4 Gly : 1 Cu Sample=2g Cu DI=500ml, Initial pH=9, Peroxide=8.3 3 ml 0.5%	1.00	0.89	22.22	0.90	22.54	0.89	22.14	0.89	22.30
	3.00	0.97	24.25	0.97	24.14	0.98	24.56	0.97	24.32
	6.00	0.97	24.24	0.97	24.25	0.99	24.66	0.98	24.39
	24.00	0.96	23.93	0.93	23.14	0.94	23.47	0.94	23.51
	48.00	0.99	24.78	0.99	24.69	0.99	24.79	0.99	24.75
	72.00	0.99	24.76	0.99	24.75	0.98	24.56	0.99	24.69

Table 24 /4 gly : 1 Cu Initial pH=10/

Leaching Conditions	Time, hrs	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	Ave [Cu], g/L	Ave % Cu extraction
4 Gly : 1 Cu Sample=2g Cu DI=500ml, Initial pH=10, Peroxide=8.3 3 ml 0.5%	1.00	0.96	24.01	0.94	23.50	0.97	24.13	0.96	23.88
	3.00	0.98	24.61	0.95	23.80	0.99	24.79	0.98	24.40
	6.00	0.97	24.24	0.97	24.14	0.96	24.11	0.97	24.16
	24.00	1.07	26.77	1.05	26.24	1.08	27.10	1.07	26.70
	48.00	1.11	27.63	1.08	27.10	1.12	27.90	1.10	27.54
	72.00	1.13	28.37	1.12	27.90	1.16	29.00	1.14	28.42

Table 25 // 4 gly : 1 Cu /

Leaching Conditions	Time, hrs	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	Ave [Cu], g/L	Ave % Cu extraction
4 Gly : 1 Cu Sample=2g	1	0.21	5.31	0.20	4.90	0.23	5.80	0.21	5.34
	3	0.41	10.18	0.39	9.80	0.47	11.80	0.42	10.59

Cu DI=500ml, Initial pH=11, Peroxide=8.3 3 ml 0%	6	0.72	17.89	0.73	18.14	0.68	17.12	0.71	17.72
	24	1.07	26.65	1.07	26.78	1.10	27.40	1.08	26.94
	48	1.20	30.01	1.24	31.00	1.27	31.80	1.24	30.94
	72	1.30	32.52	1.34	33.40	1.34	33.44	1.32	33.12

Table 26 /4 gly : 1 Cu pH=11, peroxide 1% /

Leaching Conditions	Time, hrs	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	Ave [Cu], g/L	Ave % Cu extraction
4 Gly : 1 Cu Sample=2g Cu DI=500ml, Initial pH=11, Peroxide=8.3 3 ml 1%	1	0.52	12.93	0.54	13.50	0.50	12.54	0.52	12.99
	3	0.68	16.99	0.70	17.60	0.66	16.41	0.68	17.00
	6	0.79	19.69	0.81	20.15	0.76	19.10	0.79	19.65
	24	1.04	26.10	1.09	27.15	1.06	26.55	1.06	26.60
	48	1.17	29.30	1.22	30.45	1.16	28.90	1.18	29.55
	72	1.27	31.70	1.30	32.49	1.24	30.90	1.27	31.70

Table 27 / Sulfuric acid leaching concentration/

Leaching Conditions	Time, hrs	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	[Cu], g/L	% Cu extraction	Ave [Cu], g/L	Ave % Cu extraction
2 H2SO4 : 1 Cu /6.2 g/Sample=2 g Cu in 667 g ore, DI=500ml, Peroxide 0.5 %, 100 rmp	1	1.08	27.00	1.06	26.50	1.22	30.40	1.12	27.97
	3	1.50	37.50	1.58	39.40	1.52	38.10	1.53	38.33
	6	1.68	42.00	1.80	45.00	1.82	45.40	1.77	44.13
	24	2.04	50.91	2.02	50.60	2.09	52.14	2.05	51.22
	48	2.25	56.25	2.28	57.10	2.33	58.14	2.29	57.16
	72	2.40	60.00	2.52	63.00	2.50	62.45	2.47	61.82

Excel file attached instead of inserting all tables