

RECOVERY OF COPPER FROM OXIDE COPPER ORE BY FLOTATION AND
LEACHING

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ABSTRACT

RECOVERY OF COPPER FROM OXIDE COPPER ORE BY FLOTATION AND LEACHING

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The aim of this study was the recovery of copper from the oxide copper ore by froth flotation and agitating sulphuric acid (H_2SO_4) leaching. The ore with 4.21% copper grade used in this study was obtained from Çorum-Dangaz region of Turkey. Native copper, cuprite (Cu_2O), tenorite (CuO), and malachite ($Cu_2(OH)_2/CO_3$) were the main copper minerals in the test sample. Quartz, calcite, illite, chlorite, and plagioclase were determined as the main gangue minerals of the sample. The mesh of grind size of copper minerals was determined as 75 microns after examination of ground particles under microscope. During the flotation tests; the effects of type and dosage of collectors, pH, and dosage of activator Na_2S were examined. Results of flotation tests were unsuccessful in terms of both recovery and grade of concentrate product. The highest copper recovery of concentrate was found as 61.35% with 8.69% copper content. The concentrate with highest copper grade of 34.65% was obtained with only 26.98% copper recovery. Unsuccessful flotation of the test sample was due to unfavorable morphologic properties of native copper particles. Agitating leaching experiments were also conducted with representative sample. The effects of various parameters, such as particle size, leaching duration, acid concentration, and pulp density on extraction of copper were examined. Agitating

leaching test results were indicated that approximately 90% of copper extraction was possible. Three hours of leaching duration, 1 N sulphuric acid concentration and 100% -250 microns feed size were determined as optimum leaching conditions.

Keywords: Copper Minerals, Flotation, Agitating Leaching

ÖZ

OKSİTLİ BAKIR CEVHERİNDEN FLOTASYON VE LİÇ İLE BAKIR KAZANIMI

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Bu çalışmada oksitli bakır cevherinden flotasyon ve karıştırmalı sülfürik asit (H_2SO_4) liç yöntemleri ile bakırın kazanılması amaçlanmıştır. Deneysel olarak kullanılan % 4.21 Cu tenörlü cevher Dangaz-Çorum yöresinden alınmıştır. Nabit bakır, kuprit (Cu_2O), tenorit (CuO) ve malakit ($Cu_2(OH)_2/CO_3$) deney numunesindeki başlıca bakır mineralleridir. Kuvars, kalsit, illit, klorit ve plajyoklaz ise cevherdeki başlıca gang mineralleri olarak belirlenmiştir. Öğütülmüş tanelerin mikroskop ile yapılan incelenmesi sonucunda bakır minerallerinin ekonomik serbestleşme boyutu 75 mikron olarak belirlenmiştir. Test numunesiyle yapılan flotasyon deneylerinde toplayıcı cinsi ve miktarının, pH'nın ve canlandırıcı olarak kullanılan Na_2S miktarının etkileri araştırılmıştır. Flotasyon deneyleri ile tenor ve verim açısından başarılı bir sonuç alınamamıştır. % 8.69 tenörlü bir bakır konsantresi için en yüksek verim % 61.35 olurken, % 34.65 bakır tenörlü konsantre ancak % 26.98 gibi düşük bir verimle elde edilebilmiştir. Başarısız flotasyon test sonuçları nabit bakır taneciklerinin flotasyon için uygun olmayan morfolojik özelliklerinden kaynaklanmıştır. Temsili numunelerle yapılan karıştırmalı liç deneyleri sırasında, tane boyutunun, liç süresinin, asit konsantrasyonunun ve pülp yoğunluğunun etkileri araştırılmıştır. Optimum koşullar olarak belirlenen 3 saatlik liç süresinde, -250

mikronluk tane boyutuna sahip numuneyle 1 N'lik sülfirik asit kullanılarak yapılan karıştırma liç işlemi sonucunda % 90 oranında bakır kazanılabileceği anlaşılmıştır.

Anahtar Kelimeler: Bakır Mineralleri, Flotasyon, Karıştırma Liç

To My Lovely Family

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CHAPTER 1

INTRODUCTION

1.1 General Remarks

Copper is the name of a metallic element with an atomic number of 29. The name 'Copper' comes from 'Cyprium' which means the metal of Cyprus where the mining of the copper began. Copper is being mined for thousands of years and it is a vital metal of mankind with very high electrical and thermal conductivity. Copper has many different end uses from industry to home applications. Main end uses of copper are; electrical equipment and products such as motors, generators, electrical cables, and transformers, building and construction materials such as plumbing, valves, fittings, transportation, used in motor vehicles, aircrafts, trains, and ships, and industry such as machinery, equipment. Copper is mined by both underground and open pit mining methods and served to global economy after being processed with various mineral beneficiation techniques. Copper ore bodies are divided into three separate groups which are native copper ores, sulphide copper ores, and oxide copper ores. Most important copper beneficiation techniques are froth flotation, gravity separation, and acid leaching processes. Usually sulphide copper ores are processed by froth flotation whereas oxide copper ores are treated with acid leaching processes globally. In the first part of this study, froth flotation of copper ore with hydroxamate type collectors and traditional flotation after sulphidisation by using sulphhydryl type collectors was tried. In the second part of the study, agitating sulphuric acid leaching process was applied on the test sample.

1.2. Objective and Scope of the Thesis

Oxide copper minerals were uneconomic since near history because of the adequate supply of high grade sulphide minerals. However, now oxide copper minerals will be mined and processed under economic aspects with the increase in the demand of copper metal. In this study, froth flotation and acid leaching behaviors of the test sample which is composed of native and oxide copper minerals were examined in order to find out the optimum conditions for copper recovery.

CHAPTER 2

LITERATURE REVIEW

2.1 Copper

2.1.1 Copper and Its Properties

Copper is a transition metal with a chemical symbol Cu. Copper has an atomic number of 29 and an atomic weight of 63.546. Copper is composed of two stable isotopes which are copper 63 with 69.17% and, copper 65 with 30.83%. Copper belongs to Group 1B of the periodic table. Pure copper has a structure of face centered cubic crystalline structure having a density of 8.96 g/cm³ at 20 °C. Melting point of copper is 1083 °C whereas the boiling point of copper is 2567 °C (Salem Press Encyclopedia of Science, 2013).

2.1.2 Copper Minerals and Origin of Copper

Copper occurs in nature as native copper Cu or in minerals as copper sulphides like chalcopyrite and chalcocite, the copper carbonates like azurite and malachite, and copper oxides like cuprite. There are more than 170 copper bearing minerals known 10 to 15 of which are economically being mined. Most important copper bearing minerals are tabulated in Table 1 below.

Table 1: Copper Bearing Minerals

Name	Formula	Copper %
Chalcopyrite	CuFeS_2	34.5
Chalcocite	Cu_2S	79.8
Covellite	CuS	66.5
Bornite	$2\text{Cu}_2\text{S}\cdot\text{CuS}\cdot\text{FeS}$	63.3
Tetrahedrite	$\text{Cu}_3\text{SbS}_{3+x}(\text{Fe,Zn})_6\text{Sb}_2\text{S}_9$	32-45
Malachite	$\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$	57.3
Azurite	$2\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$	55.1
Cuprite	Cu_2O	88.8
Chrysocolla	$\text{CuO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$	37.9
Enargite	Cu_3AsS_4	48.41
Tennantite	$\text{Cu}_{12}\text{As}_4\text{S}_{13}$	51.6
Tenorite	CuO	79.75

Copper is found in various concentrations in Earth's lithosphere, hydrosphere, atmosphere, and pedosphere. Approximately 5% of the copper found in the lithosphere is found in sedimentary rocks especially in shale whereas only 0.00004% in soil. 0.001% of the copper found in the lithosphere can be mined under economic conditions and some of it has been mined for centuries (Salem Press Encyclopedia of Science, 2013).

2.1.3 Copper Reserves

2.1.3.1 World Copper Reserves

Copper today is generally being mined from the oxide and sulphide zones of copper ore bodies. According to United States Geological Survey report, world has a total copper ore reserve of 690,000,000 tons. Distribution of these ore reserves are given in Table 2 below (U.S. Geological Survey, 2012).

Table 2: World Copper Reserves by Countries (U.S. Geological Survey, 2012)

<u>Countries</u>	<u>Reserves as Metal (Tons)</u>
Australia	87,000,000
Canada	10,000,000
Chile	190,000,000
China	30,000,000
Congo	20,000,000
Indonesia	28,000,000
Kazakhstan	7,000,000
Mexico	38,000,000
Peru	70,000,000
Poland	26,000,000
Russia	30,000,000
Turkey	3,700,000
United States	39,000,000
Zambia	20,000,000
Other Countries	91,300,000
World Total	690,000,000

In Table 3 below, global copper ore production is tabulated (U.S. Geological Survey, 2012). In 2006 top 3 copper producing countries were Chile, United States, and Peru whereas in 2012 the list has changed that the top three copper producing countries became Chile, China, and Peru.

Table 3: Global Annual Copper Productions by Countries in 2012 (U.S. Geological Survey, 2012)

Rank	Country/Region	2012 Copper Production (tonnes)	Rank	Country/Region	2012 Copper Production (tonnes)
1	 Chile	5,433,900	14	 Iran	245,200
2	 China	1,642,300	15	 Brazil	219,600
3	 Peru	1,298,564	16	 Laos	149,580
4	 United States	1,170,000	17	 Argentina	135,700
5	 Australia	914,000	18	 Papua New Guinea	125,348
6	 Russia	720,000	19	 Mongolia	123,900
7	 Zambia	629,020	20	 Bulgaria	118,255
8	 DR Congo	608,400	21	 Turkey	101,700
9	 Canada	578,586	22	 Spain	97,636
10	 Mexico	500,275	23	 Sweden	82,422
11	 Poland	427,064	24	 South Africa	81,000
12	 Kazakhstan	424,000	25	 Uzbekistan	80,000
13	 Indonesia	398,100			

World demand for copper sharply increases in case of global expanding. With the increase of this demand, supply should also increase in parallel in order to keep the copper market stable. In Figure 1 below, annual copper ore production of the world is presented. (Brown, et al., 2014)

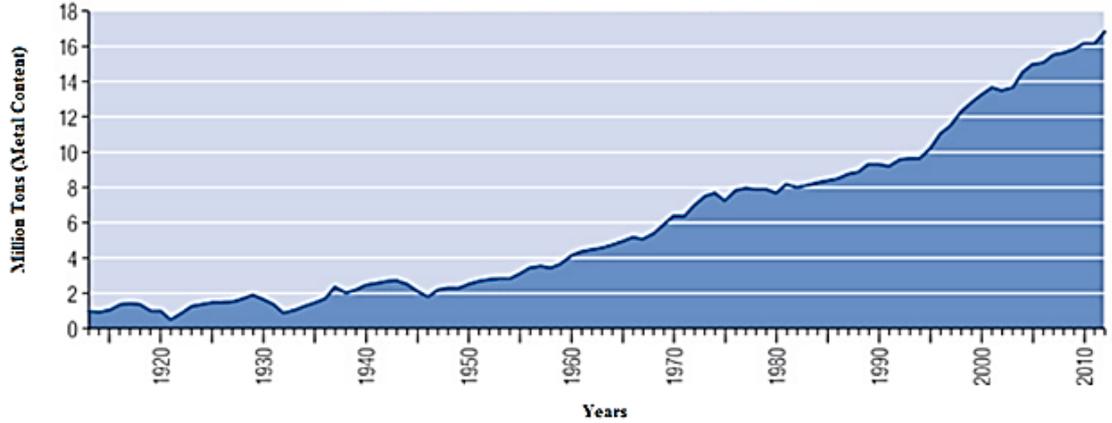


Figure 1: World Annual Copper Production (Brown et al., 2014)

As seen from the Figure 1 above, there is a slight increase in metal copper production from the year 2010 (16,100,000 tons) to the year 2012 (16,800,000 tons).

2.1.3.2 Turkey Copper Reserves

Sulphide copper ores, oxide copper ores, and native copper ores are found in Turkey. Eti Bakır A.Ş. which is a subsidiary of Cengiz Holding A.Ş., Çayeli Bakır İşletmeleri A.Ş. which is a subsidiary of First Quantum Minerals Ltd., and Park Elektrik Üretim Madencilik Sanayii ve Ticaret A.Ş. which is a subsidiary of Ciner Holding A.Ş. are the leading copper ore producers in Turkey. Çayeli Bakır is expected to mill 1,200,000 tons of copper ore from Çayeli Underground Mine in 2014 and produce copper concentrate containing 27,000-29,000 tons of copper in 2014 (First Quantum Minerals Ltd., 2014). Park Elektrik produced 89,253 tons of copper concentrate with an average copper content of 18% to 20% copper from Madenköy Mine in 2012 (Mobbs, 2014). Turkey's copper ore production in 2012 was 7,400,000 tons of run-

off mine which had a copper content of 100,000 tons and Turkey's smelter output in 2012 was 25,000 tons (Mobbs, 2014).

Turkey has a copper reserve of 3,700,000 tons of metal copper while total reserves amount is 15,800,000 tons which are located in the East Black Sea and South East Anatolia regions (General Directorate of Exports, 2014).

2.1.4 Uses of Copper

Copper is being used since the ancient times and it was one of the first metals which were used by mankind because of its occurrence in nature as a pure metal and its ductility that can be worked by hand easily. It is estimated that pure copper was mined and used by mankind around 8000 B.C. Since those days, copper has protected its importance while being a component of important materials like pewter, brass, and bronze. Copper was the second mostly used metal in the world after the Industrial Revolution while the most used metal was iron. Aluminum discovery has made copper less useful in modern days because of its availability and properties. Copper is used in the electrical industries mostly because of its high ductility and high electrical conductivity. Copper can be electrolytically refined up to 99.62% pureness. Remaining material will be oxygen primarily helping to the conductivity of the copper wire and its density to be increased. Another use of copper is construction industry and electrical industry in the shape of sheets or smaller strips made by rolling hot copper. In earlier time, copper was used in order to produce bronze which was the alloy of copper and arsenic. In modern days, copper and tin are alloyed to produce bronze which is used in ornaments, musical instruments, and bells. Moreover, copper and zinc are alloyed in order to produce brass which has a wide range of hardness, ductility, and malleability used for industrial purposes. Copper and nickel are alloyed in various concentrations producing many alloys with different physical properties and industrial applications. Addition of nickel in concentrations of 2% to 45% produces harder material than copper in pure state. Moreover, addition of 20% nickel to copper results in an extremely ductile material which can be worked cold without annealing. This material is used for drop forging, pressing, cold stamping, fittings in automotive industry, and bullet sheathing. Monel metal, an alloy

of copper and nickel, is another use of copper in industry which is extremely strong at various temperatures and it is used at many different engineering applications. Furthermore, copper containing compounds have different uses in industry. For example, cuprous oxide is an antifouling agent which is used in some paints giving a red color. Moreover, cupric chloride is used in the production of some pigments while cupric oxide giving a green color to glass. Another use of copper is the form of copper sulphate which is used as desiccant and used for the manufacturing of electrolytically refined copper. Furthermore, copper compounds with arsenic are used as insecticides. Finally, like many other compounds of copper, copper carbonates are used in pigment production by imparting blue or green colors in which solutions they are used (Salem Press Encyclopedia of Science, 2013).

2.2 Froth Flotation

Froth flotation is applied on copper minerals since 1905 and many new approaches are gained up to present. There are many researches from those days to today, and many new approaches on froth flotation are examined successfully. In this section, background of the evolution of the froth flotation applied for both oxide and native copper minerals will be underlined.

Froth flotation is the most important copper processing technique applied in mineral processing industry throughout the world. Froth flotation was patented in 1906 originally permitting the mining of complex ores with low-grade content of economic minerals which would have otherwise been regarded as uneconomic (Wills, 2006). Nearly 2 billion tons of ore were treated worldwide by froth flotation until today showing that the froth flotation process is obviously one of the most important applications of surface chemistry controlling of the solid-liquid interface.

The main idea of the froth flotation process is the concentration of finely divided minerals on the basis of variations keeping themselves on a phase interface. Moreover, by these conditions, the particles which need to be separated from others float up and removed in some way, together with the phase they are attached. Froth flotation tests are carried out in an aqueous medium which is called as the first phase

whereas the other phase is air or some other gas or, much more rarely oil (Glembotskii et al., 1972). Froth flotation uses the differences in physical and chemical surface properties of minerals to be separated from each other. After treatment with different reagents of froth flotation experiments, surface property differences between the minerals and the bubbles become much more apparent and, an air bubble must be able to attach itself to a particle and lift it up to the water surface in order to take place flotation activity (Wills, 2006).

In Figure 2 below, principles of froth flotation is shown in a simple sketch of mechanical froth flotation cell. The agitator at the bottom of the cell provides sufficient turbulence in the pulp phase in order to ensure the collision of particles and bubbles resulting in the attachment of valuable particles with bubbles and transportation of them into the froth phase to recover the desired minerals (Wills, 2006).

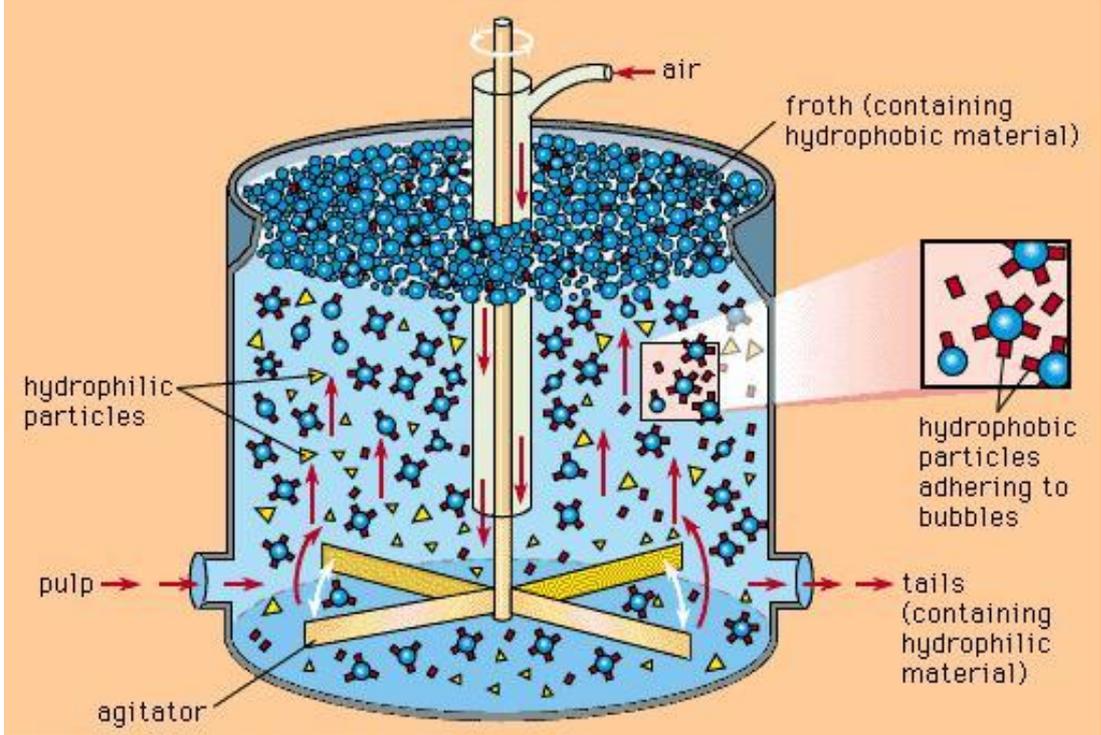


Figure 2: Froth Flotation Cell (Encyclopedia Britannica, 2014)

Successful froth flotation separations are dependent to selective interaction between solid particles and gas bubbles in aqueous media. Controlling the interaction of mineral surfaces with water molecules with additions of various reagents and pH control mechanisms has a vital importance in froth flotation processes of making selective mineral separations from the complex ores of vast tonnages. The froth flotation has evolved over the century by empirical developments which mean that froth flotation has not come with an outcome of fundamental research. Most of the basic research done for the froth flotation technology has been occupied with explaining why the existing processes works so well. Much of the basic research done for mineral processing technology and process metallurgy can be defined as post-modern researches or as Fleming and Kitchener (1965) says “science in pursuit of technology”. Progress in fundamentals of froth flotation has been based on experimental investigations made in laboratories, combining sharp knowledge into the meaning of the data found (Parekh & Miller, 1999).

First applied flotation enrichment technique for copper minerals is known to be applied on the recovery of sulphide minerals from ores, resulting in all of the published research in early time was conducted on sulphide minerals, especially galena, sphalerite, chalcocite, chalcopyrite, and pyrite (Fuerstenau et al., 2007).

With the new developments of the technology and increasing demand of copper, oxide copper ores have become economical to be mined and processed. The most important industrially beneficiated copper minerals among the oxide copper ores are as follows; malachite with chemical formula $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, copper content of 57.4% Cu, and azurite with chemical formula $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, copper content of 55.2% Cu, whereas the less important ones are; chrysocolla with chemical formula $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ and copper content of 36.1% Cu, cuprite with chemical formula Cu_2O and copper content of 88.8% Cu (Glembotskii et al., 1972)

Many researchers believe that the froth flotation of oxide copper ores is a complex mineral processing method and it first needs the sulphidisation stage. According to Ge et al. (2013), oxide copper minerals have thick hydration film surfaces which are hard to contact with air bubbles meaning flotation of them has been below sulphide copper ores technically and economically. Moreover, oxide copper ore enrichment

with low dissolution rates generally utilizes froth flotation method after sulphidisation stage or mixture of flotation and hydrometallurgy or flotation-segregation, whereas oxide copper ores with high dissolution rates are generally processed by hydrometallurgical processing.

From the beginnings of the development of froth flotation, generally sulphide copper ores are beneficiated in economic ways whereas oxide caps of these sulphide ore bodies are leaved as gangue because they were uneconomic to be processed. Depletion of copper sulphide ores worldwide and the increase of the demand for copper ores in industry resulted in starting to mine the copper oxide ores and processing them in order to supply the demand globally. (Xiong & Zheng, Process Mineralogy and Flotation Kinetic of a Copper Oxide Ore during Sulfuration Flotation, 2013).

According to Glembotski et al. (1972), oxide copper ores such as malachite and azurite can be successfully floated by applying sulphidisation step easily. At those years in the past, at one of the Soviet plants, 1% copper containing oxide copper ore was floated with a recovery of 80% and a copper grade of 19%.

Wills (2006) mentioned that oxide cap of primary copper deposits can be mined selectively and successfully processed by froth flotation. Furthermore, oxide copper ore flotation is now more attractive in the case of cheap sulphuric acid provided by smelters.

Nagaraj and Somasundaran (1977) worked on flotation of copper minerals. In their test work chrysocolla and quartz mixture having 2.13% Cu grade was used. Using the collector emulsion containing 0.034 kg/t Tergitol and 0.5 kg/t of LIX65N in hexane (3.0 kg/t), the rougher concentrate was obtained through 4 minutes flotation which was cleaned twice. Final concentrate with 21.3% Cu grade was obtained with the recovery of 69%.

Arakatsu et al. (1977) worked on Chilean copper oxide ore and got the patent of their work. Copper oxide ore used in test work had a grade of 2.6% copper and 0.28% sulphur. At first, ore was ground to 60% passing 200 mesh. The chemicals used in the tests were pine oil, sodium sulphide, 5-methyl benzotriazole, benzotriazole,

potassium amyl xanthate, light oil, and mobile oil No.20. A copper concentrate of 27.8% Cu grade was obtained with a recovery of 71.2%

Rule (1982) worked on an ore containing total copper of 1.77%, 1.67% of which is oxide copper and 0.10% is sulphide copper. 80% of the ore was atacamite and paracamite. Ore is ground to 97% passing 100 mesh. During the tests, pH of the pulp was 8.7. A mixture of 0.4 lb/t potassium octyl hydroxamate and 0.8 lb/t potassium amyl xanthate was added as collector and the pulp was conditioned for 20 minutes. After adding mixture of small amount of 1:1 pine oil and methyl iso butyl carbinol, a copper concentrate with copper grade of 6.88% (which has 6.52% oxide copper and 0.36% sulphide copper) was obtained with 83.86% recovery.

Twiddle and Engelbreth (1984) worked on the developments in the froth flotation of copper at Black Mountain Mineral Development Company Limited. Twiddle and Engelbreth concentrated copper ore consisting of chalcopyrite, galena, and sphalerite with 0.63% Cu. Chemicals used during flotation tests were; isopropyl ethyl thio-carbamate (24 g/t at rod mill, 16 g/t at conditioner, 6 g/t at second rougher, 4g/t at regrind mill, and 3 g/t at second cleaner), zinc sulphate (548 g/t at rod mill, and 15 g/t at conditioner), methyl iso butyl carbinol (5 g/t at conditioner, 3 g/t at first cleaner, 6 g/t at second cleaner), sulphuric acid (522 g/t at conditioners and cleaners), and lime (166 g/t at rod mill). pH was 6.3, 6.4, 5.9, 5.0, and 5.1 at conditioners, second rougher, first cleaner, second cleaner, and third cleaner respectively. A copper concentrate with 24.15% copper grade with 65% recovery was obtained.

Lee et al. (1998) reported that alkyl hydroxamate reagent has an effective result on the recovery of well-defined oxide copper minerals like malachite, cuprite, etc... Some of the acid soluble copper minerals are not applicable to flotation with hydroxamates which are copper containing goethite, finely disseminated cuprite in a gangue matrix, and chrysocollas which have very low copper contents.

Ziyadanoğulları and Aydın (2005) conducted a research on Ergani Copper Mining Co. Turkey's oxide copper ore. According to analyses of the test sample, ore contains 2.03% copper, 0.15% cobalt, and 3.73% sulphur. Researchers applied grinding of 100% passing 100 mesh and sulphidisation process. After all, potassium

amyl xanthate and Dowfroth 250 were used as flotation reagents at pH 8.7. A copper concentrate of 9.36% Cu with a recovery of 93.16% was obtained.

Lee et al. (2008) showed that hydroxamate type collectors work well on oxide copper minerals. Test work was conducted on the copper ore of Sherwood Copper's Minto Mine Yukon, Canada. According to the analyses, copper sample from the site contains 70% sulphide copper and 30% oxide copper. Total copper content of the ore was 3.6%. Methyl iso-butyl carbinol (MIBC) which was provided by Orica Mining Services was used as frothing reagent. Collectors of potassium amyl xanthate (PAX) and potassium n-octyl hydroxamate (AM28) which were provided by Tall Bennett Group and Ausmelt Chemicals respectively were used during the tests. The sulphidisation reagent, sodium hydrogen sulphide (NaHS) was sourced from Acros Organics. 2 minutes of conditioning time was allowed at pH of 8.1. The overall AM28 dosage was up to 1200 g/t and frother MIBC dosage was up to 50 g/t. In cleaning stages, an additional 100 g/t of AM28 and 50 g/t of MIBC were used. After flotation process a copper concentrate with a grade of 33.9% copper and with a recovery of 78.5% was obtained. It is showed that AM 28 successfully beneficiated malachite and minor azurite, which were found in Minto's oxide ore.

Phetla and Muzenda (2010) studied an oxide copper ore from a Region in Central Africa. The ore which was worked on has a total copper grade of 4.5% which contains 88% of copper oxide minerals and 12% of sulphide, refractory, and undissolved copper. Sodium hydroxide sulphide (NaHS) as sulphidiser, potassium amyl xanthate (PAX) as sulphide collector, n-octyl hydroxamate (AM2), Oleofloat 6540, rinka lore, diesel, sodium carbonate, and tall oil as oxide collector, and alcohol based frother Dow200 were used during the study. A concentrate with 13% copper grade was obtained with 48% recovery. Author indicated that the poor response was due to high proportions of copper silicate minerals in the ore.

Xiong et al. (2012) worked on cuprite-type oxide copper with 1.29% total copper grade which was supplied by the Copper Company of Dishui Corporation, Xinjiang, China. Sodium iso-amyl xanthate (SIAX) was used as collector, sodium sulphide (Na₂S) was used as sulphidisation reagent, methyl iso butyl carbinol (MIBC) was used as frother, and ammonium sulphate ((NH₄)₂SO₄) was used as modifier. At the

end of test work, it is concluded that the use of ammonium sulphate is beneficial for the sulphidisation of the oxide copper ore. At optimum flotation conditions where a dosage of 1000 g/t $(\text{NH}_4)_2\text{SO}_4$, 1000 g/t Na_2S , 800 g/t SIAX at, and 40 g/t pinitol oil, a copper concentrate with 18.23% copper grade was obtained with 73.46% copper recovery.

Ou and Yin (2012) treated copper and cobalt ore consisting of both sulphide and oxide copper minerals. Both sodium sulphide (Na_2S) and sodium hydrosulphide (NaHS) were used in order to activate the copper oxide mineral. Amyl xanthate (AX) was used as collector reagent at roughing, scavenging, and cleaning stages. A copper concentrate with the copper grade of 21.2% was obtained with the recovery of 88.55% from the ore containing 2.63% Cu and 0.04% Co.

Xiaofeng et al. (2012) used a chelating agent which was named as KLY consisting of improved ethylene phosphate during the flotation of oxide copper ore from Yongshan, Yunnan province of China which consists of 0.88% malachite and cuprite, and 0.05% native copper. Ore was crushed and ground to 90% passing 200 mesh in comminution stage. Flotation tests were conducted with modifying agents of sodium silicate, sodium sulphide, and chelating agents KLY, collector of mixed xanthate and frother of pine oil. After 4 cleaning stages, a concentrate with 22.87% copper grade was obtained and with 83.99% recovery from the ore containing 0.55% copper.

Pang et al. (2013) worked on a copper oxide ore of Guizhou, China. In their research, ore samples containing 1.15% Cu with an oxidation rate up to 83.48% were used. Chalcopyrite, chalcocite, covellite, and bornite were the copper minerals in the ore while quartz, dolomite, and mica were main gangue minerals. After sulphidisation with 1000 g/t sodium sulphide, and collector 240 g/t YX-2, a copper concentrate with 22.13% Cu grade was obtained with a copper recovery of 88.52%

Xiong et al. (2013) treated oxide copper ore with 1.02% copper content which's 0.56% was acid soluble copper from Yangla Mine in Yunnan province of China. Mixture of Potassium Amyl Xanthate (PAX) and a hydroxamate AM28 were used as

collectors. It is reported that a rougher concentrate with a grade of 3.19% was obtained with 38.4% copper recovery at the end of the test work.

Ge et al. (2013) treated copper oxide ore containing 0.77% Cu from the Yunnan province of China. The main metal minerals in the ore were hematite, pyrite, bornite, covellite, and malachite. Quartzite, dolomite, plagioclase, chlorite, and calcite were reported as the main gangue minerals in the ore. By using butyl xanthate (90 g/t) as collector, pine oil (35 g/t) as frother, sodium sulphide (1000 g/t) as sulphidisation agent, and lime (3000 g/t) as pH regulator, with three stages of cleaning, a concentrate with 18.06% copper grade was obtained with recovery 80.81%.

Wang et al. (2013) worked on a copper oxide ore from Dali, Yunnan province of China. Test samples contain 0.69% of copper and 11.24 g/t of silver. Ore was beneficiated by sulphidisation and xanthate flotation method. The flotation tests were carried out systematically with sodium sulphide as sulphidisation agent and butyl xanthate and ammonium dibutyl dithiophosphate as the combined collectors. Applying closed circuit tests, a copper concentrate with 18.34% of copper grade and a recovery of 70.13% was obtained.

Xiong et al. (2014) stated that the alkyl-hydroxamate-based chelating reagents show excellent flotation performance for the copper oxide minerals. The chelating reagents used in the flotation of oxide copper ores can be classified according to their type of atoms that bond to the metal cations and participate in the closure of the chelate ring. N-O type chelating collectors are unsuitable for the flotation of chrysocolla, but this type of collectors work well on malachite. O-O type chelating reagents give satisfactory results for native copper, and an important hydroxamate, namely potassium n-octyl hydroxamate or AM28 developed by Ausmelt, has been used in current productions showing itself to be an excellent collector for oxide copper minerals and native copper over a wide pH range, and it is highly effective for the flotation of chrysocolla with pH range of between 7 to 10. S-N type chelating agent phenylthiourea is a highly active collector for flotation of chalcopyrite, native copper, covellite, melaconite, and cuprite, whereas it is ineffective for copper carbonate and chrysocolla.

2.3 Sulphuric Acid Leaching Process

Acid leaching is one of the widely used processes for the extraction of copper metal from complex oxide copper ores. Heap leaching of metallic ores is a well-proven process, especially in the copper industry where many millions of tons of cathode copper have been produced using solvent-extraction and electro-winning for many years in a cheaper way. In its simplest method, the acid heap leach process consists of building a large heap of crushed ore and irrigating the surface of the heap with a dilute solution of acid. As the acid permeates through the heap, it dissolves the metals in the ore which are taken into solution. The pregnant solution is collected at the bottom of the heap, usually on an impermeable rubber liner, and pumped away for further treatment using various chemical processes dictated by the metal being recovered and the chemical constituents of the ore. Figure 3 below shows a simple sketch of the heap leaching process.

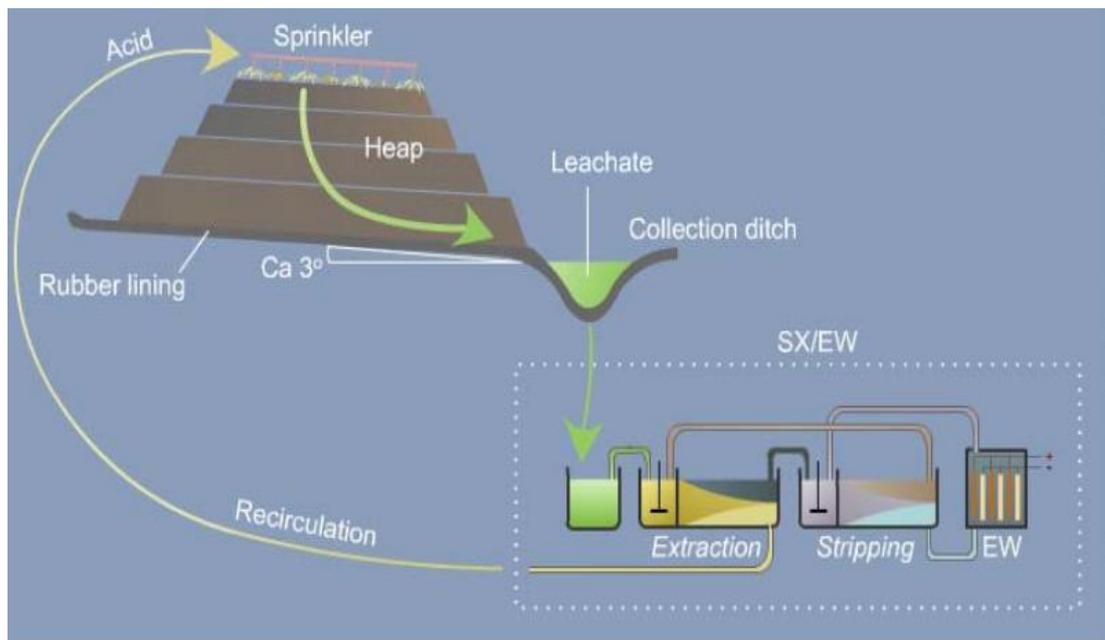


Figure 3: Heap Leaching Process. (Vest et al., 2009)

There is an extensive literature on acid leaching process for refractory ores especially for oxide copper ores because of their complexity for applications of froth flotation. Table 4 below shows the list of copper minerals encountered during leaching of copper ores in the order of amenability to leaching.

Table 4: Main Copper Minerals Encountered in Leaching of Copper Ores

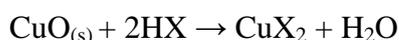
Copper Minerals	Chemical Formula
Malachite	$\text{Cu}_2\text{CO}_3(\text{OH})_2$
Azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
Cuprite	Cu_2O
Chrysocolla	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$
Chalcocite	Cu_2S
Covellite	CuS
Bornite	Cu_5FeS_4
Chalcopyrite	CuFeS_2

During sulphuric acid leaching processes it is important to optimize the total process according to the reaction times. Reactions which are commonly encountered in sulphuric acid leaching processes are tabulated in Table 5.

Table 5: Common Reactions Encountered in Sulphuric Acid Heap Leaching (Innovat Limited)

<u>Fast Reactions:</u>	
Copper Oxide	$\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$
Malachite	$\text{Cu}_2\text{CO}_3(\text{OH})_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{CuSO}_4 + 3\text{H}_2\text{O} + \text{CO}_2$
Chrysocolla	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 3\text{H}_2\text{O} + \text{SiO}_2$
<u>Medium Reactions:</u>	
Chalcocite	$\text{Cu}_2\text{S} + \text{H}_2\text{SO}_4 + 0.5\text{O}_2 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O} + \text{CuS}$
Bornite	$\text{Cu}_5\text{FeS}_4 + 2\text{H}_2\text{SO}_4 + 9\text{O}_2 \rightarrow 5\text{CuSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{O}$
<u>Slow Reactions:</u> (Requiring Oxidation of Sulphide)	
Chalcopyrite	$\text{CuFeS}_2 + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 2\text{FeSO}_4 + \text{FeS} + \text{S}^0$
	$\text{S}^0 + \text{H}_2\text{O} + 1.5\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$
	$2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + 0.5\text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$

Habbache et al. (2009) worked on the enrichment of oxide copper ores by acid leaching process. Different acid solutions which are hydrochloric acid, sulphuric acid, nitric acid, and citric acid were used in order to examine the effects of different parameters such as stirring speed, temperature, and acid concentrations. The following reaction takes place on Copper (II) Oxide;



Where, the X indicates NO_3 , Cl, and SO_4 .

The study was ended with a satisfactory result of copper recovery of 99.95% with inorganic acids at 0.5 M, at 25 °C, and solid to liquid of 1:10 (g/ml).

Vest et al. (2009) pointed out the importance of heap leaching on copper extraction. It is reported that the 20% of the world copper production is done by hydrometallurgical leaching processes generally by leaching oxide copper ores with

the use of sulphuric acid and subsequent solvent extraction and electro-winning processes. 100 ppm nonionic surfactant called EVD61549 was used as solvent to extract copper from the pregnant solution of diluted sulphuric acid. Finally, 75.58% of copper was recovered at the end of the tests.

Zhong et al. (2009) worked on copper oxide ore from Mexico. The test sample was containing both copper oxide and copper sulphide minerals. Initially flotation technique was applied and a copper concentrate with 19.01% Cu grade was obtained with 35.02% copper recovery. During the flotation tests, the reagents of sodium sulphide and butyl xanthate were used. After processing the tailings of flotation process by leaching under the conditions of; 60 minutes leaching time, 500 rpm stirring speed, 25 °C room temperature, 1N H₂SO₄ concentration, and 1:3 solid to liquid ratio, copper recovery was increased to 83.33%.

Chao et al. (2013) worked on the copper oxide ore with a low copper content of 0.71%. Test sample was containing 51% copper oxide minerals. By froth flotation and acid leaching, it is tried to get a copper concentrate. With sulphidisation and flotation processes, a copper concentrate with 15.02% Cu grade was obtained with a recovery of 38.55%. In the case of sulphuric acid tests under the optimum conditions of 120kg/ton sulphuric acid, 4:1 liquid to solid ratio, 120 minutes leaching duration, 500 rpm stirring speed, 20 °C temperature, 78.75% of the copper in the ore was recovered. By applying the leaching process to tailings of flotation processes, copper recovery was increased up to 86.85%.

Kordosky (2002) published a paper showing the improvements in acid leaching technology. In the paper, an example from Ranchers' Bluebird sulphuric acid leach/solvent extraction/electrowinning plant was given. According to the paper, copper oxide ore with a copper grade higher than 0.5% was heaped in 6 meter height. Dilute sulphuric acid was distributed over the ore by spraying. As the heaps are processed with sulphuric acid, new heaps were built on old heaps. Pregnant leach solution was collected from the pond which was built with a dam near the heap. After heap leaching process, 36 g/l Cu, 3 g/l Fe, and 145 g/l H₂SO₄ was entered to electrowinning cells resulted with an efficiency of 80 to 85%. Moreover it is reported that at several oxide heap leach operations copper recoveries were around 85%.

CHAPTER 3

EXPERIMENTAL MATERIAL AND METHODS

3.1 Materials

Throughout this thesis study, copper ore from Dangaz region of Çorum was used. Ore deposit has a probable reserve of 1 million tons. Flotation experiments were carried by using the collectors of CYTEC Industries Inc.. Leaching experiments were carried out by using analytical grade sulphuric acid solutions of Merck Company.

3.1.1 Characterization of Sample

Approximately 50 kilograms of ore sample is taken by channel sampling method from the coordinates of Y: 593043, X: 4505940 in Dangaz region, Çorum (Figure 4). Representative sample of the ore deposit is provided by Köseoğlu Madencilik İnşaat Sanayii ve Ticaret A.Ş.. Sample provided contains native and oxide copper minerals, and throughout the experiments same sample is used.



Figure 4: Location of the Ore Deposit

In order to determine the general characteristics of the ore sample, chemical and mineralogical characterizations were performed. The complete chemical analyses of the representative test sample were done with X-Ray Fluorescence spectrophotometer (XRF) and Atomic Absorption Spectrophotometer (AAS) methods. Firstly, whole sample was reduced to -2mm with the help of jaw and roll crushers. A representative sample was obtained from this crushed ore by coning and quartering method. Crushed sample was wet screened. The results of the screen analysis are presented in Table 6. The crushed test sample was reduced to -38 microns for chemical analyses. The chemical analyses results of the ore used in the experiments are given in Table 7.

Table 6: Wet Screening Analyses Results

Size Fractions	Weight (%)	Cu Grade (%)	Cu Distribution (%)
-2mm + 74 μ m	10.23	4.92	11.79
-74 μ m + 53 μ m	51.31	4.07	48.91
-53 μ m + 38 μ m	29.55	4.20	29.07
-38 μ m	8.91	4.30	10.23
Total	100	4.27	100

As seen from the Table 6, there are no significant differences between the copper grades of various size fractions.

Table 7: Chemical Analyses of Representative Ore Samples

Component	Weight %
Cu	4.21
SiO ₂	52.54
Al ₂ O ₃	13.89
CaO	7.96
Fe ₂ O ₃	4.40
MgO	3.60
TiO ₂	0.72
K ₂ O	1.76
MnO	0.14
Na ₂ O	0.11
P ₂ O ₅	0.14
Loss of Ignition	10.4
Others	0.13

X-Ray Diffraction Spectrometry (XRD) was also applied in this study to analyze the mineral composition of the test sample. For analysis, ore samples ground to 100% passing 38 microns were used. The peaks of the diffraction were recorded and plotted against a horizontal scale in degrees of 2θ , which is the angle of the detector rotation in order to catch the diffracted X-Ray.

The XRD pattern of the sample is given in Figure 5. The XRD pattern of test sample indicated that the ore is mainly made up of quartz, calcite, illite, chlorite, and plagioclase minerals as gangue.

Peak Search

Sample : 15F-random File : 15F-random.ASC Date : June-18-14 12:18:00 Operator :
 Comment : A.G.Turkmenoglu Memo : Gonca Alptekin
 Method : 2nd differential Typical width : 0.087 deg. Min. height : 656.46 counts

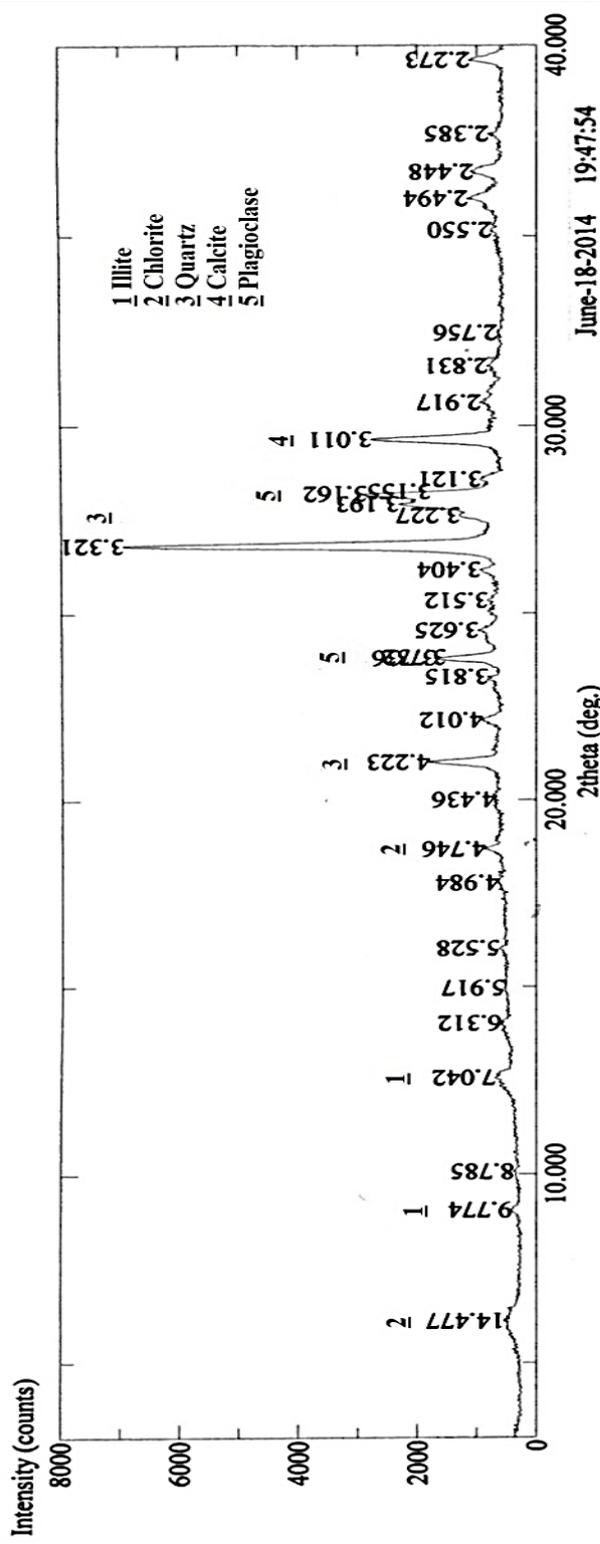


Figure 5: XRD Pattern of Test Sample

Under microscope, representative feed was examined which was ground to 100% passing 75 microns. It is seen that native copper minerals are squashed and pasted to relatively coarse and plate like particles with sharp edges and corners (Figure 6). Mineralogical analyses also show that native copper and malachite were the major copper minerals in the test sample.

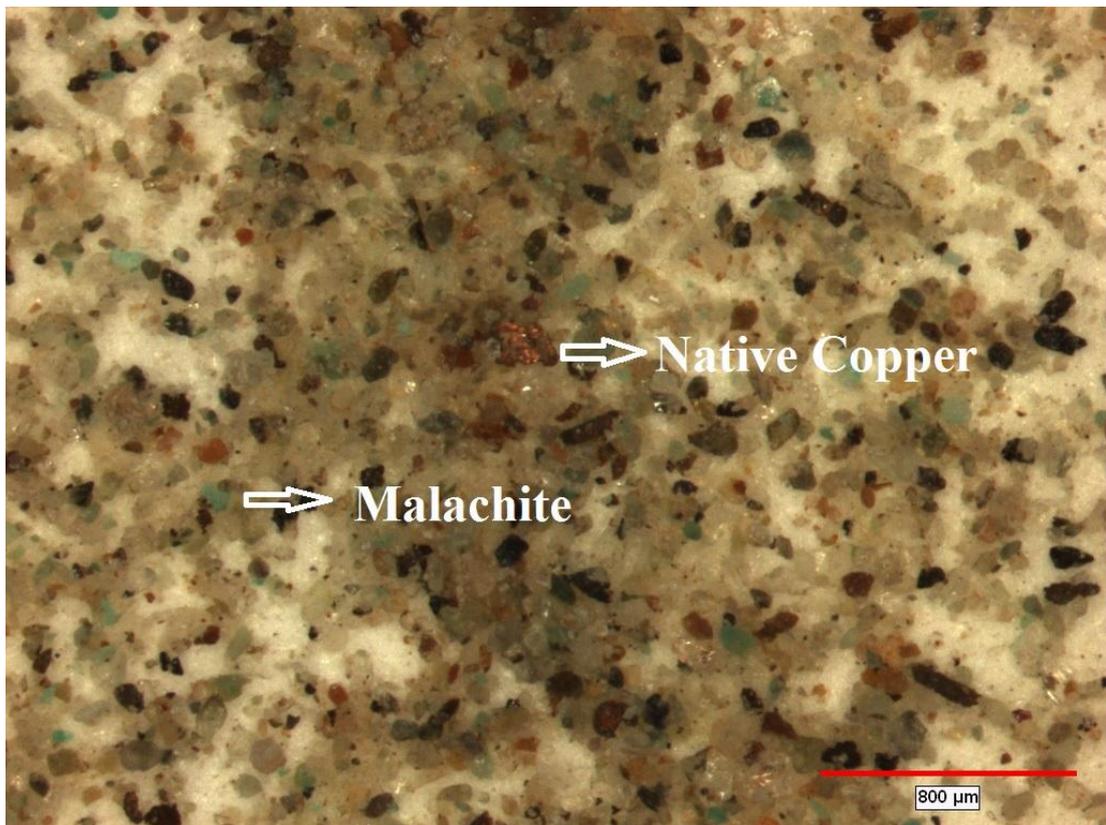


Figure 6: View of Ground Test Sample Under Microscope

3.2 Methods

In this study, froth flotation and agitating sulphuric acid leaching methods were applied in order to find the optimum operating conditions which give highest recoveries. Methods followed during the experimental study will be discussed in detail in the proceeding sections.

3.2.1 Materials Sampling

In this study two different size laboratory jaw crushers and a roll crusher were used in order to crush the material from 10 cm size down to 100% passing 2mm size. -2 mm ore was introduced into different size riffles and divided into two equal parts, riffing procedure was repeated until a desired sample size for the experiments was achieved.

3.2.2 Flotation Experiments

A number of flotation tests were performed in order to study the influence of various flotation parameters. Parameters studied were the fineness of feed, type and dosages of collectors, dosage of Na_2S , and pulp pH.

The flotation test work was carried out by using Denver-Sub A laboratory flotation machine with a 1-liter glass cell (Figure 7). During the flotation tests, METU tap water was used. Chemical analyses of METU tap water is given in Appendix A.



Figure 7: Denver-Sub A Laboratory Flotation Machine

Flotation reagents were dissolved in distilled water and added into flotation cell in dilute solutions. A list of reagents used in the study is shown in Table 8 below.

Table 8: Chemical Reagents Used in Flotation Tests (Cytex, 2002)

Reagents	
AERO 6493	Hydroxamate , collector
AERO 350	Potassium Amyl Xanthate (PAX), collector
AERO 3302	Xanthate Alkyl Ester, collector
AERO 407	Mercaptobenzothiazole and dithiophosphate, collector
AERO 208	(Ethyl+Butyl) Dithiophosphates, collector
AERO 3477	Isobutyl Dithiophosphates, collector
Na₂S	Sulphidisation reagent
Ca(OH)₂	pH Regulator
H₂SO₄	pH regulator
Pine Oil	Frother
MIBC	Frother

3.2.3 Preparation of Sample for Flotation Tests

Grinding of the ore is an important step in the study in order to provide the desired liberation of the valuable copper minerals. Optimum liberation size of minerals was determined after examination of various size fractions of ground product under reflected light microscope.

The mineralogical analysis of various size fractions of ground sample showed that approximately 80% of copper containing particles have been liberated below 75 microns.

-2 mm size test samples were ground in laboratory rod mill for 10 minutes, 15 minutes, and 20 minutes to determine the grinding time in order to reach the mesh of grind size. The results of grinding tests are tabulated in Tables 9, 10, 11, and presented in Figure 8.

Table 9: Sieve Analysis of 10 Minutes Ground Sample

10 Minutes Grinding			
Sieve Size Range (μm)	Weight (%)	Cumulative Oversize (%)	Cumulative Undersize (%)
+250	0,71	0,71	99,29
-250 +150	2,35	3,06	96,94
-150 +106	16,15	19,21	80,79
-106 +75	19,29	38,50	61,50
-75 (pan)	61,50	100,00	
Total	100,00		

Table 10: Sieve Analysis of 15 Minutes Ground Sample

15 Minutes Grinding			
Sieve Size Range (μm)	Weight (%)	Cumulative Oversize (%)	Cumulative Undersize (%)
+250	0,25	0,25	99,75
-250 +150	0,11	0,36	99,64
-150 +106	0,80	1,16	98,84
-106 +75	8,92	10,08	89,92
-75 (pan)	89,92	100,00	
Total	100,00		

Table 11: Sieve Analysis of 20 Minutes Ground Sample

20 Minutes Grinding			
Sieve Size Range (μm)	Weight (%)	Cumulative Oversize (%)	Cumulative Undersize (%)
+250	0,07	0,07	99,93
-250 +150	0,04	0,11	99,89
-150 +106	0,31	0,42	99,58
-106 +75	2,05	2,47	97,53
-75 (pan)	97,53	100,00	
Total	100,00		

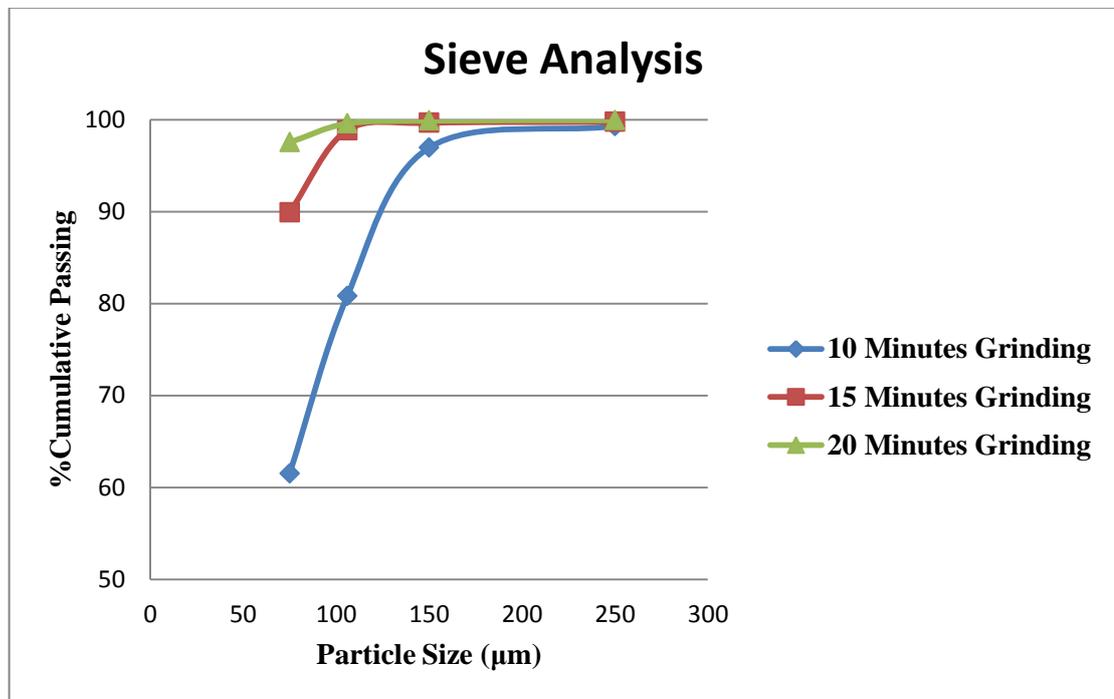


Figure 8: Effects of Grinding Time on Size Distribution of Ground Product

Grinding test results showed that for 15 minutes of grinding, 90% of particles were passed through 75 microns. In the following flotation tests 90% -75 microns size feed material was used.

In this study, a laboratory rod mill produced by Denver Company is used. It has geometry of 19.5 cm inner diameter and 31 cm length (Figure 9). During the grinding tests, 250 grams ore sample, 250 ml tap water and 4 pieces of 2.54 cm diameter and 8 pieces of 1.84 cm diameter rods were used (Figure 10).



Figure 9: Laboratory Rod Mill

Flotation tests were conducted with 90% passing 75 microns size material. The solid-water mixture was prepared at desired pulp density in a one-liter glass cell. After adjustment of pH, collector was added and the pulp was conditioned for five minutes. A frother was then added and after 30 seconds of conditioning, the air valve was turned on and produced froth was skimmed into a stainless steel tray until a visible froth collection ceased. The concentrate and tailing products were dried in electrical oven at 105 °C. The dried products were weighed and analyzed for their copper contents.



Figure 10: Grinding Mill Charge

3.2.4 Agitating Leaching Experiments

Agitating leaching experiments were carried out with the experimental set-up shown in Figure 11. Leaching test set-up consisted of a magnetically stirred hot plate with temperature controller and a 500 ml glass beaker. The agitating sulphuric acid leaching tests were conducted with 50 grams of test samples. In the study 100% - 1000 microns, 100% -500 microns, and 100% -250 microns feed materials were tested to see the effect of particle size on leaching. Prepared leach solution of known volume at the desired sulphuric acid concentration was placed into the glass beaker, and then 50 grams of ground ore sample was added into the beaker and stirred at a constant speed by a magnet to obtain sufficient mixing during the desired leaching period. Leach solution is then filtered by a vacuum pump using a suitable filter paper (Figure 12). In order to determine the leachability of the ore with sulphuric acid under atmospheric pressure, the parameters such as the effects of particle size, acid concentration, pulp density, and leaching duration were examined.



Figure 11: Agitating Sulphuric Acid Leaching Experimental Setup



Figure 12: Vacuum Filter

3.2.5 Assaying of Products

There is no difference in the assaying method of the flotation concentrates and assaying method of leach residues. Analyses were carried out on dried products by using Atomic Absorption Spectrophotometer in METU Mineral Processing Laboratory.

1 gram of flotation product or leach residue were taken and dissolved with 10 ml aqua regia ($3\text{HNO}_3 + \text{HCl}$) solution in a beaker and was put on the hot plate at 100°C until yellow colored vapor finishes. Then, by washing with distilled water, the solution in the beaker was filtered through Scheicher and Schuell Micro Science 589/1 Black Ribbon filter paper (Figure 13). After being filtered, copper analyses were done by atomic absorption spectrophotometer (AAS) (Figure 14).



Figure 13: Filtering of the Solution

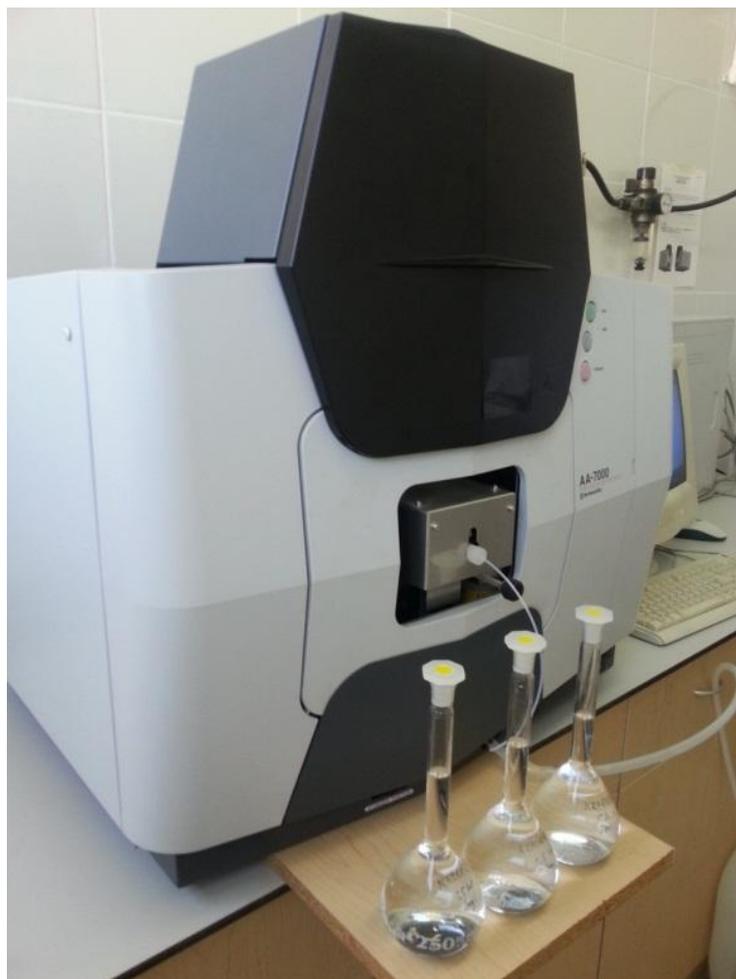


Figure 14: Atomic Absorption Spectrophotometer (AAS)

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Flotation with Hydroxamates

First group of flotation tests were carried out with the hydroxamate AERO 6493. The effects of pH and collector dosage were examined during the experiments.

4.1.1 Effect of pH

The natural pH of the pulp was 7.0. NaOH and H₂SO₄ were used as pH regulators. During the flotation tests, the effect of pH was examined at the pH range from 6 to 13. The results of the experiments are shown in Table 12 and Figure 15 below.

Table 12: Effect of pH on Flotation

Flotation pH	Cu % in Concentrate	Recovery (%)
6	3.93	6.43
7	5.73	10.93
8	10.09	26.43
9	17.62	22.14
10	5.70	15.60
11	4.65	12.45
12	3.77	8.78
13	3.9	7.94

Operational Data:

Collector: AERO 6493

Collector Dosage: 100 g/ton

Frother: 50 g/ton Pine Oil

Conditioning Time: 5 min.

Flotation Time: 3 min.

Impellor Speed: 1035 rpm

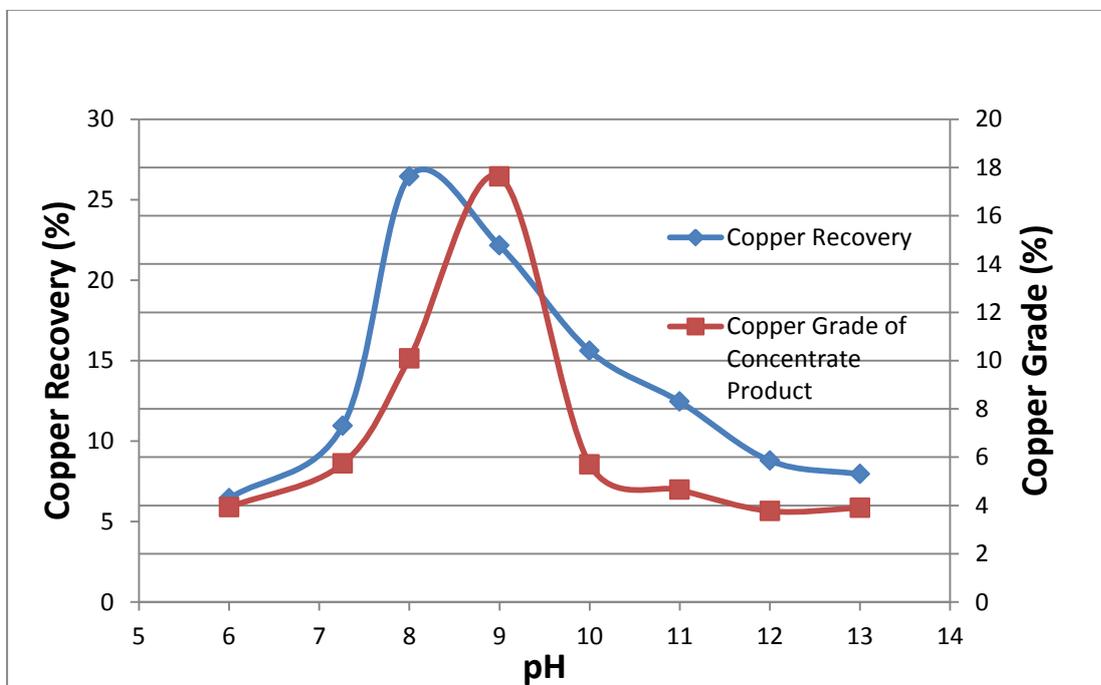


Figure 15: Effect of pH on Copper Recovery and Copper Grade of Concentrate

It is seen from Table 12 and Figure 15 that although maximum grade and recovery was obtained in the pH range of 8.0 to 9.0, both grade and recovery of copper concentrates were very low at all examined pH values.

4.1.2 Effect of Collector Dosage

In order to see the effect of collector dosage on copper recovery and copper grade, flotation experiments were carried out with varying collector dosages. During these tests to increase the absorption of collector on particle surface, conditioning time was increased to 10 minutes and kept as constant. The results are tabulated in Table 13 and presented in Figure 16.

Table 13: Effect of Hydroxamate Dosage on Flotation

AERO6493 Dosage (g/ton)	Copper Grade (%)	Copper Recovery (%)
200	9.55	52.2022
400	11.25	51.6180
800	13.80	57.4550
1000	10.04	61.2243
1500	7.16	68.0132
2000	5.91	67.7347
3000	5.06	67.2297

Operational Data:

Conditioning Time: 10 min.

Flotation Time: 3 min.

pH: 9

Frother: 50 g/ton Pine Oil

Impeller Speed: 1035 rpm

The results show that up to a collector dosage of 1500 g/ton, there is an increase in the recovery of copper in the concentrate product. However, further increase in the dosage of collector did not make any increase on the copper recovery of the concentrate.

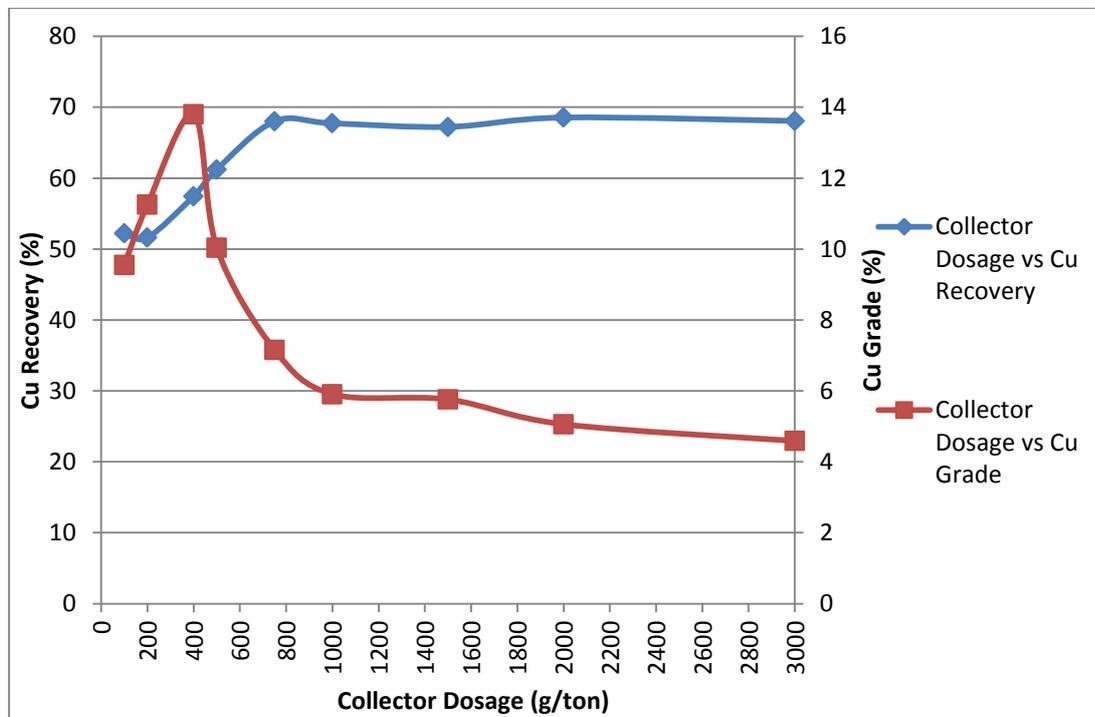


Figure 16: Effect of Hydroxamate Concentration on Copper Recovery

At the end of the flotation tests which are carried out with hydroxamate type of collectors, it is concluded that the hydroxamate type of collectors are not effective on flotation of the test sample.

4.2 Flotation after Sulphidisation

Oxide copper minerals do not respond well to traditional flotation using known sulphhydryl type collectors without activation. Recovery of oxide copper minerals by froth flotation requires sulphidisation with sodium sulphide (Na_2S), sodium hydrosulphide (NaHS) or ammonium sulphide ($(\text{NH}_4)_2\text{S}$). In this study, sodium sulphide (Na_2S) was used as sulphidisation agent.

4.2.1 Effect of Collector Type

Five different sulphhydryl type collectors namely Potassium Amyl Xanthate (PAX), AERO 3302 (Isoamyl Dithiophosphate), AERO 407 (Mercaptobenzothiazole + Dithiophosphate), AERO 208 (Ethyl + Buthyl Dithophosphate), and AERO 3477 (Isobutyl Dithiophosphate) were used after sulphidisation stage. Flotation experiments were carried out at room temperature and natural pH of the pulp. During the initial flotation experiments, Na₂S dosage (500 g/ton), sulphidisation period (5 minutes), dosage of selected collector (150 g/ton), conditioning time for collector (5 minutes), and frother pine oil amount (50 g/ton) were kept constant. The results of these experiments are shown in Table 14 and presented in Figure 17.

Table 14: Experimental Results for Collector Selection

Collector	Cu Grade (%)	Copper Recovery (%)
PAX	22.95	30.46
AERO3302	16.94	12.63
AERO407	14.89	7.56
AERO208	20.75	15.01
AERO3477	13.25	6.26

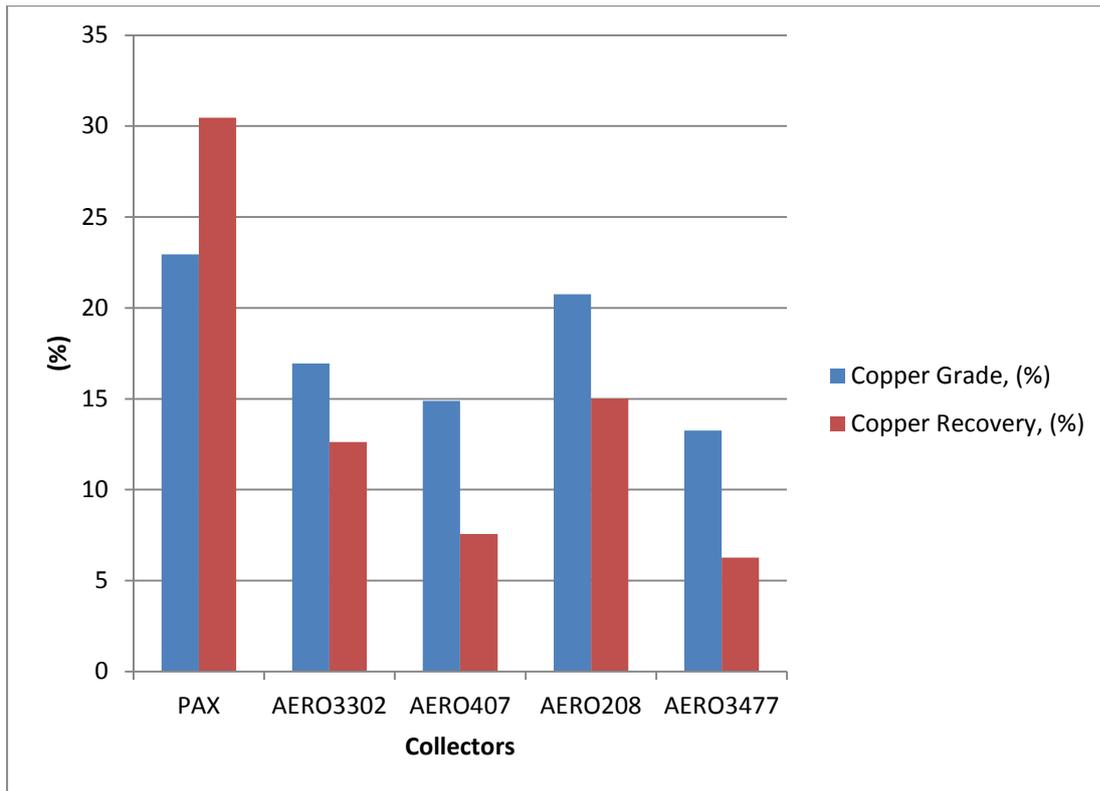


Figure 17: Effect of Collector Type on Concentrate Copper Grade and Recovery

The results of these tests showed that the copper concentrate with maximum grade and recovery was obtained with using collector Potassium Amyl Xanthate (PAX).

4.2.2 Effect of Sodium Sulphide Dosage

A group of flotation tests were carried out in order to see the effect of increase in the sulphidiser amount used. During these experiments, dosage of collector PAX (150 g/ton), pulp pH (natural), dosage of frother pine oil (50 g/ton), conditioning time for sulphidisation agent (5 minutes), and conditioning time for collector PAX (5 minutes) were kept constant. The results of these tests were tabulated in Table 15 and presented in Figure 18. According to the test results, it is seen that copper grade is directly proportional to sodium sulphide dosage whereas copper recovery is inversely proportional to sodium sulphide dosage up to 1500 g/ton.

Table 15: Effect of Sodium Sulphide Dosage on Grade and Recovery of Copper

Na_2S (g/ton)	Copper Grade (%)	Copper Recovery (%)
500	22.95	30.4556
1500	34.34	27.1894
2000	34.65	26.9751

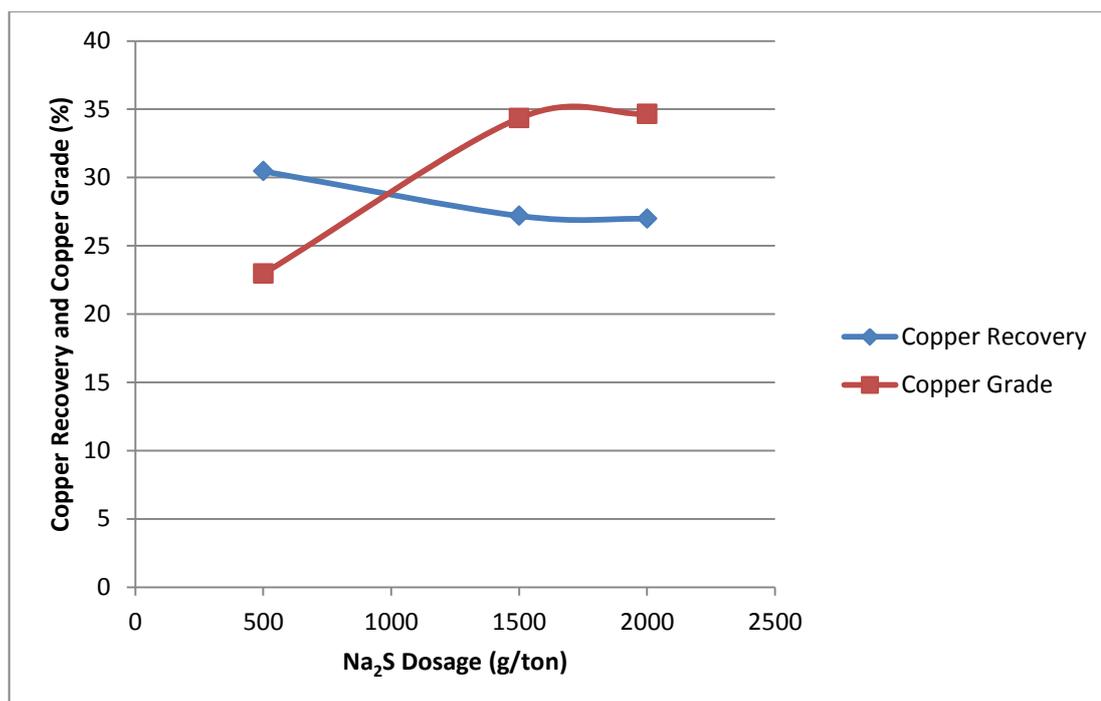


Figure 18: Effect of Sodium Sulphide Dosage on Grade and Recovery of Copper

4.2.3 Effect of Potassium Amyl Xanthate Dosage

A group of flotation tests were carried out in order to see the effect of increase in potassium amyl xanthate (PAX) dosage. The flotation recoveries of copper as a function of PAX dosage were tabulated in Table 16 and presented in Figure 19 below. During these experiments, dosage of Na_2S (1500 g/ton), pH (natural), pine oil dosage (50 g/ton), conditioning time for sulphidisation agent (5 minutes), and conditioning time for collector PAX (5 minutes) were kept constant. According to the test results, it is seen that copper recovery is directly proportional to potassium

amyl xanthate dosage whereas copper grade is inversely proportional to potassium amyl xanthate dosage up to 750 g/ton.

Table 16: Effect of PAX Dosage on Recovery of Copper Minerals

PAX Dosage (g/ton)	Copper Grade (%)	Copper Recovery (%)
150	34.65	26.98
250	31.89	29.48
500	30.98	37.67
750	30.45	43.15

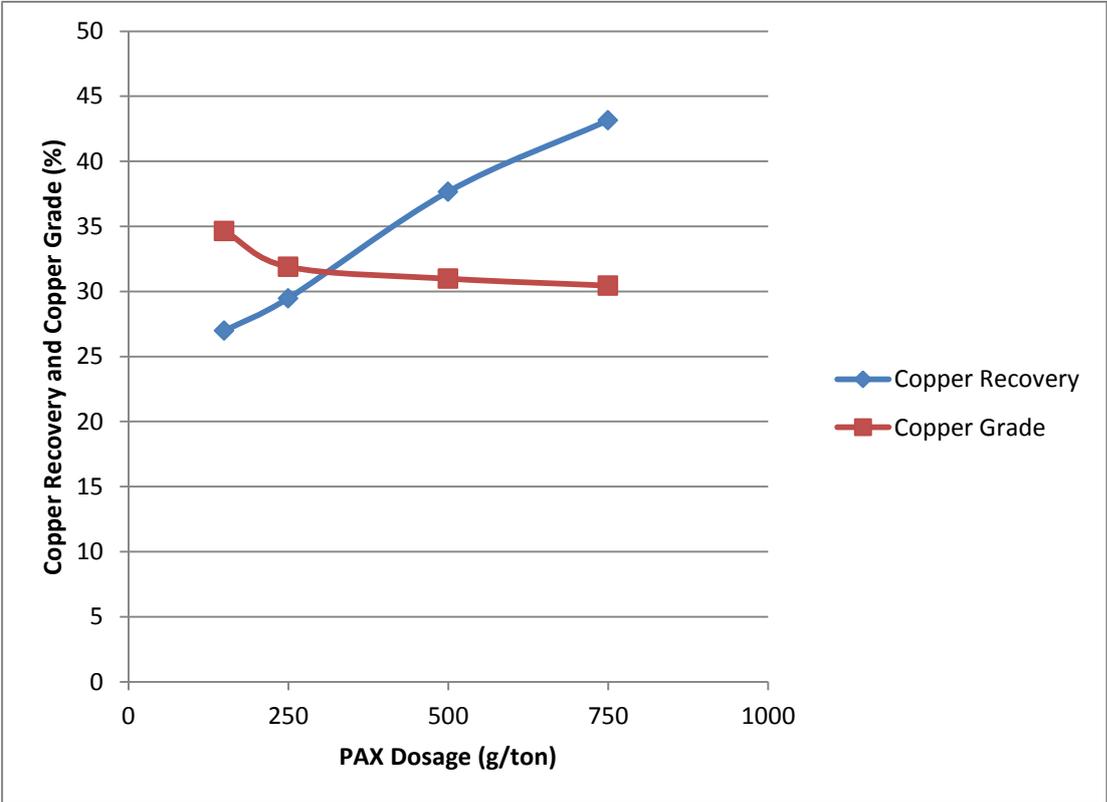


Figure 19: Effect of PAX Dosage on Grade and Recovery of Copper Minerals

4.2.4 Two-Stage Flotation of Test Sample

A group of two-stage flotation tests were carried out by using two different types of collectors at each stage. First stage of the flotation test was carried out by using hydroxamate type collector (1500 g/ton AERO 6493). After removal of froth, sodium sulphide (Na_2S) (500 g/ton) was introduced into residual pulp prior to addition of Potassium Amyl Xanthate (PAX) (150 g/ton) and another froth product was removed. A copper concentrate which is a combination of two froth products was obtained with 61.35% copper recovery and 8.69% copper grade. Figure 20 shows the flow sheet followed during this flotation test. Although there was an increase in the recovery of copper, grade of the concentrate was not suitable for the market.

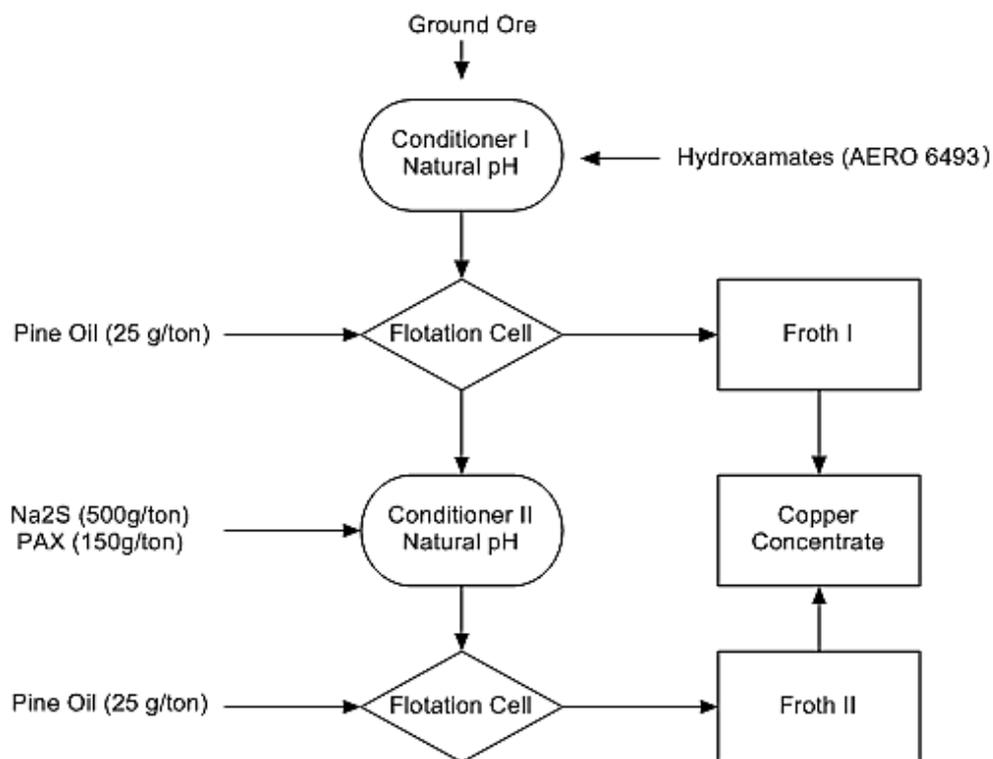


Figure 20: Two-Stage Flotation of Test Sample

At the end of the flotation tests, it is concluded that flotation is not a promising method for recovery of copper from the test sample. The low recovery of the copper was due to native copper content of test sample. This conclusion is drawn after the

examination of flotation tailing product. Considerable amount of native copper particles and malachite mineral particles were detected in tailing product (Figure 21). It is known that copper is a malleable metal and, during the grinding of test sample native copper particles squashed and pasted to relatively coarse and plate like particles with sharp edges and corners. This morphologic property of particles was not suitable for attachment of air bubbles and cause bursting of air bubbles. The sizes of relatively coarse native copper particles also adversely affect the carrying capacity of air bubbles. High amounts of malachite particles in flotation tailing indicated unfavorable behavior of malachite mineral for flotation method.

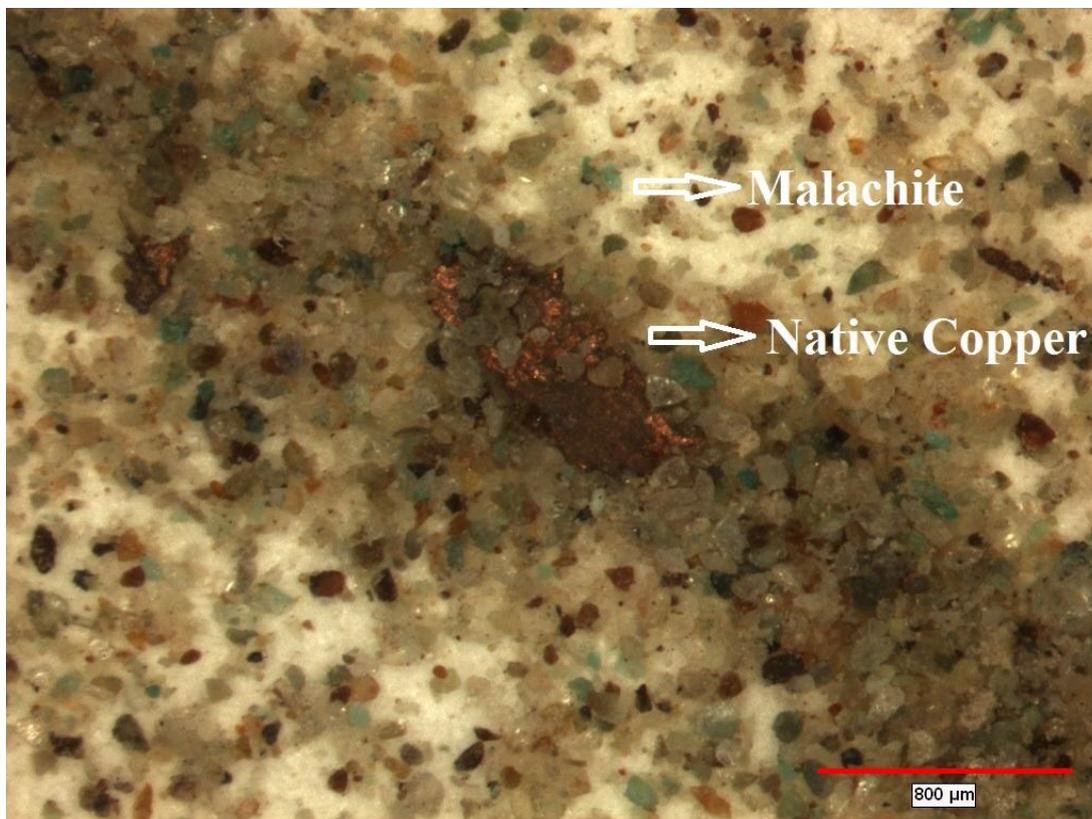


Figure 21: View of Flotation Tailing Under Microscope

4.3 Sulphuric Acid Leaching Experiments

In this part of the study, the main objective was to investigate the leachability of the ore with agitating sulphuric acid leaching method as an alternative to froth flotation.

For this purpose, a series of tests were carried out. These tests enabled to find out the leaching behaviors of the representative ore samples in different time periods, particle sizes, acid concentrations, and pulp densities. The results of leaching tests are presented in the following sections.

4.3.1 Effect of Leaching Duration

In order to see the effect of leaching duration on copper extraction, several leaching tests were carried out for 15, 30, 60, 120, 180, and 360 minutes. During these tests, weight of sample (50 g), particle size of the representative sample (100% -1mm), solid to liquid ratio (1:5 g/cm³), leaching temperature (room temperature), and sulphuric acid concentration (1 N) were kept constant. Copper extraction values of these tests are given in Table 17 and presented in Figure 22 below. Extraction percentages of copper were calculated by using the equation below;

$$\text{Extraction of Copper (\%)} = \left[100 - \frac{\text{Copper \% in Residue} * \text{Weight of Residue}}{\text{Copper \% in Ore} * \text{Weight of Ore}} * 100 \right]$$

Table 17: Effect of Leaching Duration on Copper Extraction

Leaching Duration (min)	Copper Extraction (%)
15	74.82
30	78.07
60	80.12
120	82.29
180	86.70
360	87.01
Leaching Conditions:	
Sample Weight: 50 grams	
H₂SO₄ Concentration: 1N	
Solid Liquid Ratio: 1:5 g/cm³	
Particle Size: 100% -1000 microns	

As it is seen from the Figure 22 below, the extraction of copper is improved with longer leaching duration. Nearly 87% of copper was leached in the experiment carried out for 360 minutes. The highest extraction was obtained in the experiment carried out for 360 minutes, it can be seen that in the first 15 minutes of leaching, 74.82 % of copper was extracted. Extraction percentage of copper stayed nearly at the same level after 180 minutes of leaching duration.

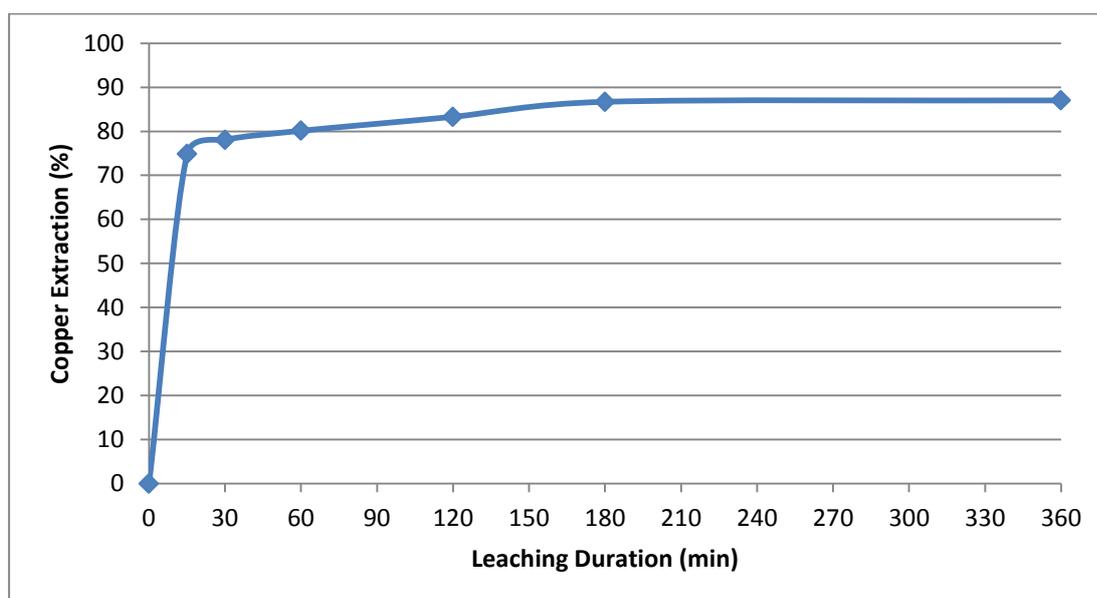


Figure 22: Effect of Leaching Duration on Copper Extraction (Feed Size: 100% - 1000 microns)

4.3.2 Effect of Particle Size

Particle size is another important parameter in leaching processes. Experiments with feed of 100% -500 microns and 100% -250 microns were carried out in order to study the effect of particle size on copper extraction. During these experiments, other parameters were kept constant (Sample Weight: 50 g, Solid to Liquid Ratio: 1:5 g/cm³, H₂SO₄ Acid Concentration: 1N). Copper extraction percentages are given in Table 18 and Table 19, and graphically illustrated in Figure 23 and Figure 24.

Table 18: Copper Extraction Percentage of 100% -500 Microns Feed

Leaching Duration (min)	Copper Extraction (%)
15	77.15
30	79.61
60	81.26
120	82.45
180	87.85
360	88.12

Leaching Conditions:

Sample Weight: 50 grams

H₂SO₄ Concentration: 1N

Solid Liquid Ratio: 1:5 g/cm³

Temperature: Room Temperature

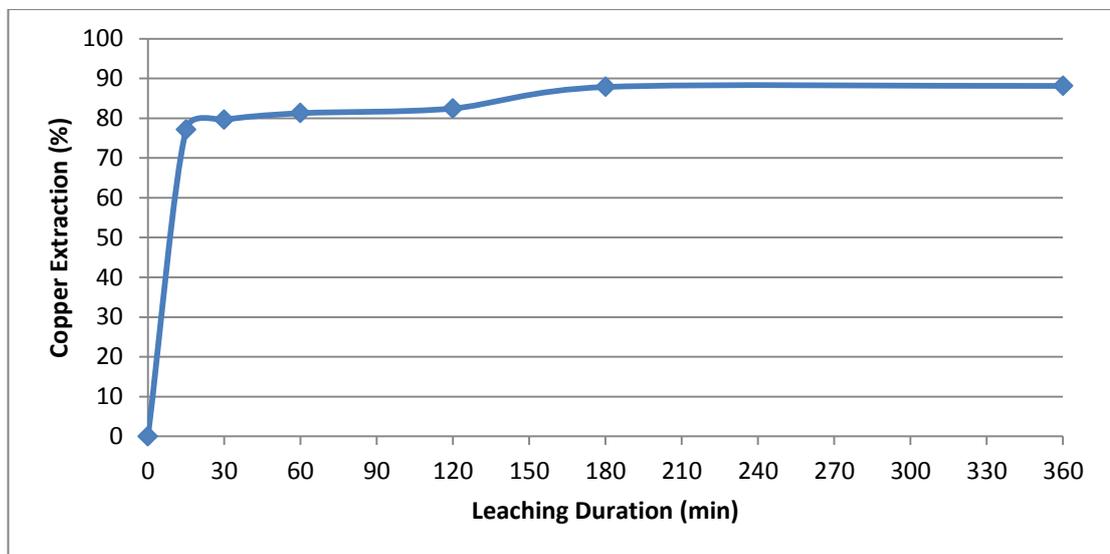


Figure 23: Copper Extraction Percentage of 100% -500 Microns Feed

Table 19: Copper Extraction Percentage of 100% -250 Microns Feed

Leaching Duration (min)	Copper Extraction (%)
15	79.04
30	81.05
60	83.55
120	85.80
180	89.11
360	89.88

Leaching Conditions:

Sample Weight: 50 grams

H₂SO₄ Concentration: 1N

Solid Liquid Ratio: 1:5 g/cm³

Temperature: Room Temperature

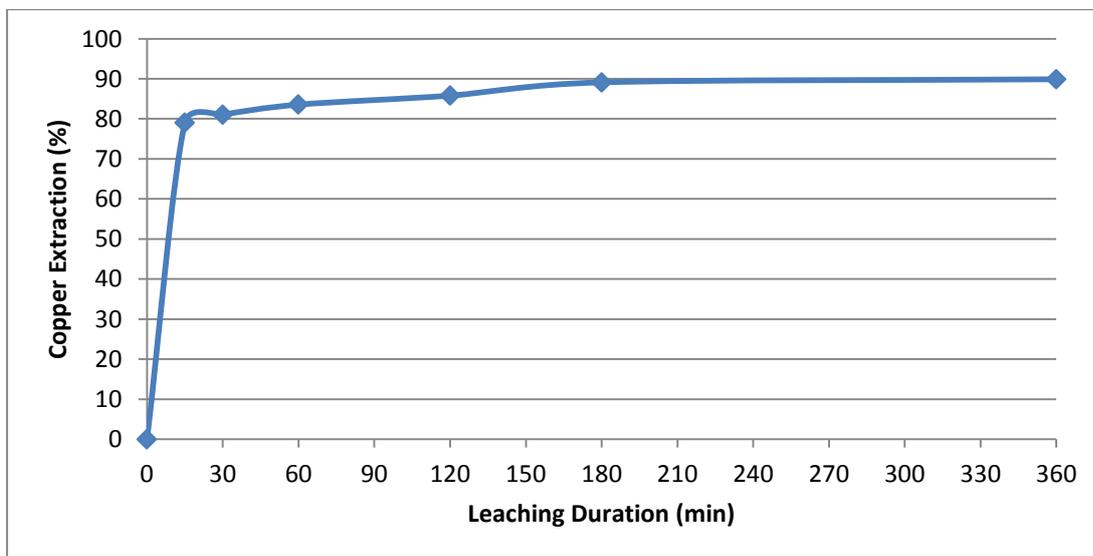


Figure 24: Copper Extraction Percentage of 100% -250 Microns Feed

The predictions prior to the experiments were that the extraction percentages would increase with the decreasing particle size of the ore. Because as the particle size increases, the interfacial area between solid particle and H₂SO₄ solution decreases

and the rate of the transfer of copper to the solution will decrease. However, the results have shown that particle size finer than 500 microns had a minor effect on copper extraction. Highest copper extraction values were obtained with the feed of 100% passing 250 microns size for all varying leaching durations (Figure 25). Therefore, further leaching tests were carried out with using 100% -250 microns size feed material.

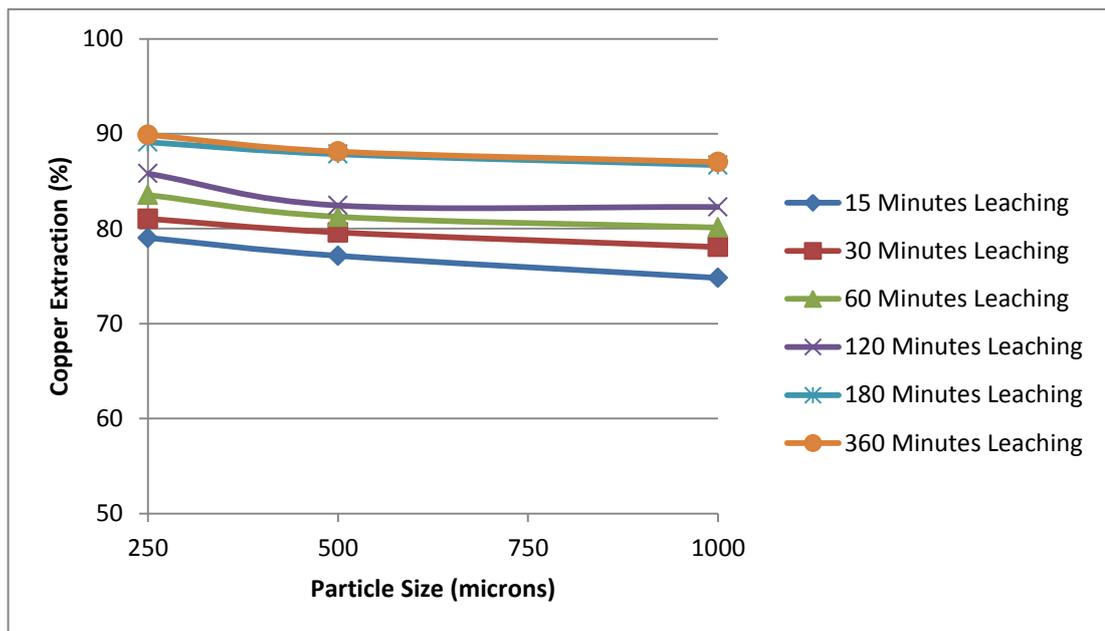


Figure 25: Effect of Particle Size on Copper Recovery

4.3.3 Effect of Acid Strength of Sulphuric Acid Solution

Acid strength of acid solution is one of the most important parameters during leaching process. In the study, four different levels of acid strength of 1N, 2N, 3N, and 4N were tested separately. During these tests, weight of sample (50 g), particle size (100% -250 microns), solid liquid ratio (1:5 g/cm³), and leaching temperature (room temperature) were kept constant. Copper extraction percentages of these tests are given in Table 20, and Figures 26, 27, 28, and 29.

Table 20: Extraction of Copper at Different Sulphuric Acid Concentrations

Sulphuric Acid Concentration	Leaching Duration (min)	Copper Extraction (%)
2N	15	80.17
	30	81.45
	60	84.58
	120	88.23
	180	90.15
	360	90.31
3N	15	82.64
	30	83.71
	60	85.49
	120	89.52
	180	91.27
	360	91.86
4N	15	85.60
	30	86.33
	60	88.49
	120	90.81
	180	91.70
	360	91.97

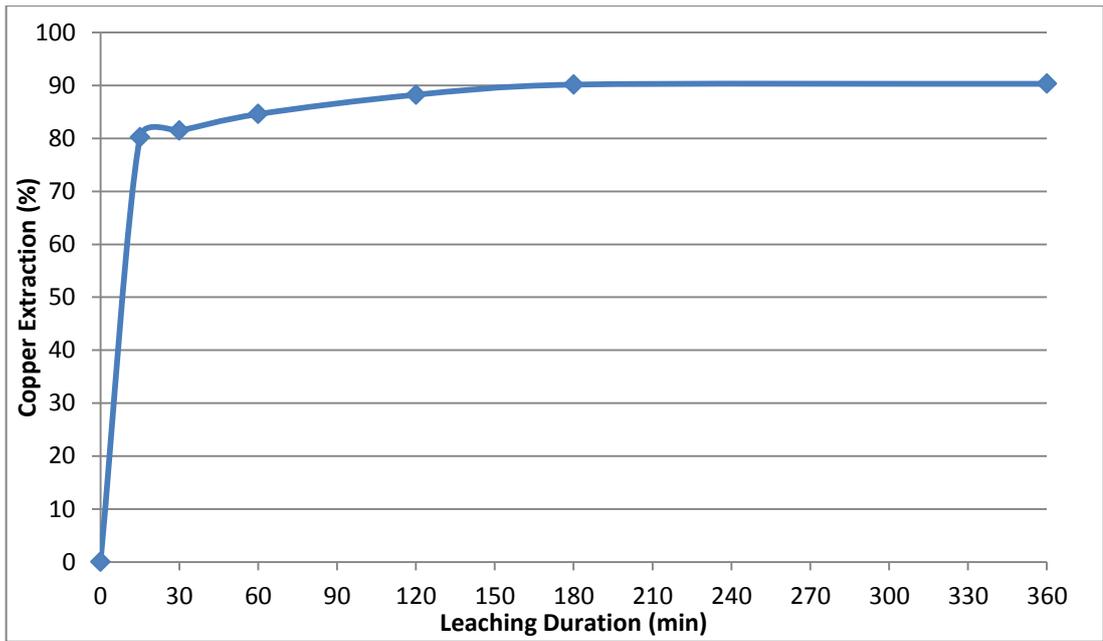


Figure 26: Copper Extraction Percentages at 2N Sulphuric Acid Concentration

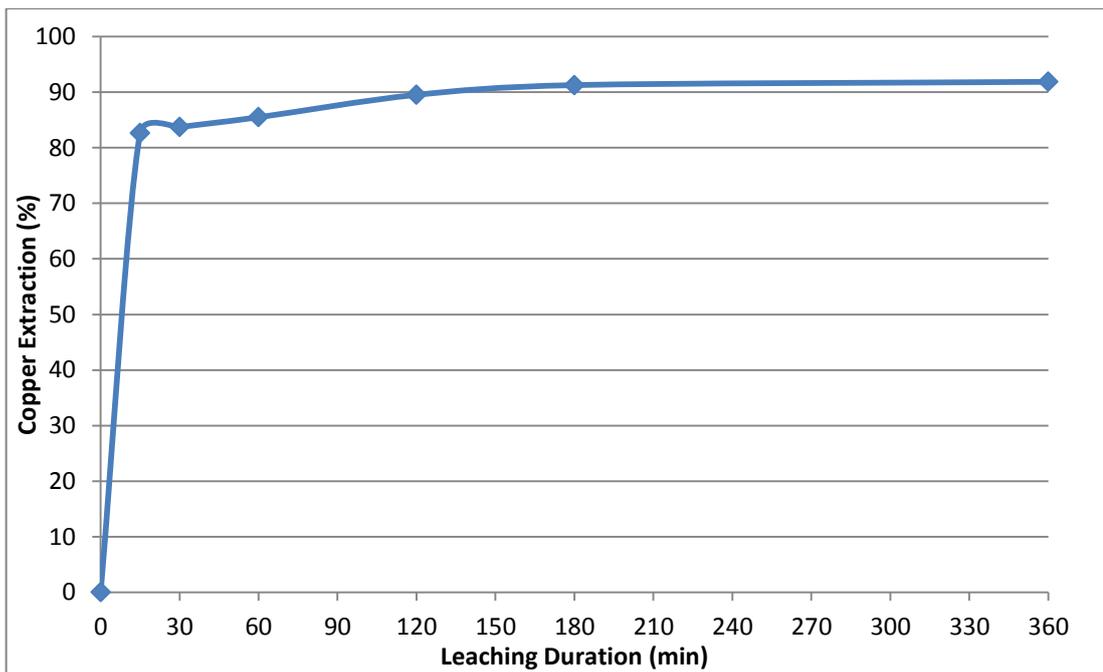


Figure 27: Copper Extraction Percentages at 3N Sulphuric Acid Concentration

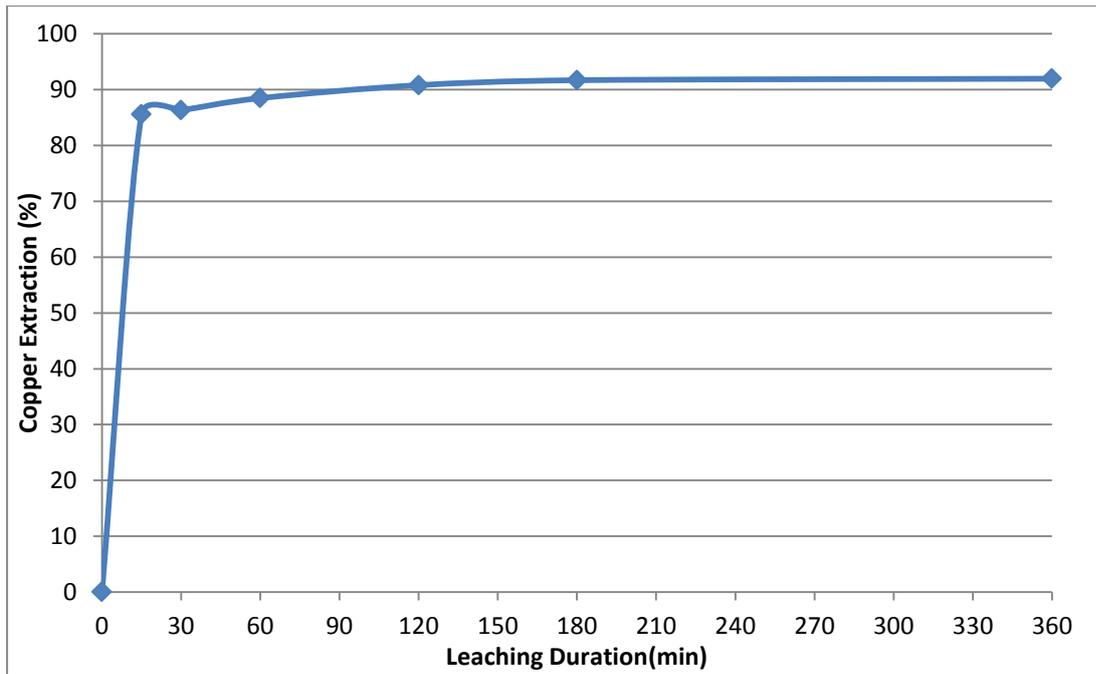


Figure 28: Copper Extraction Percentages at 4N Sulphuric Acid Concentration

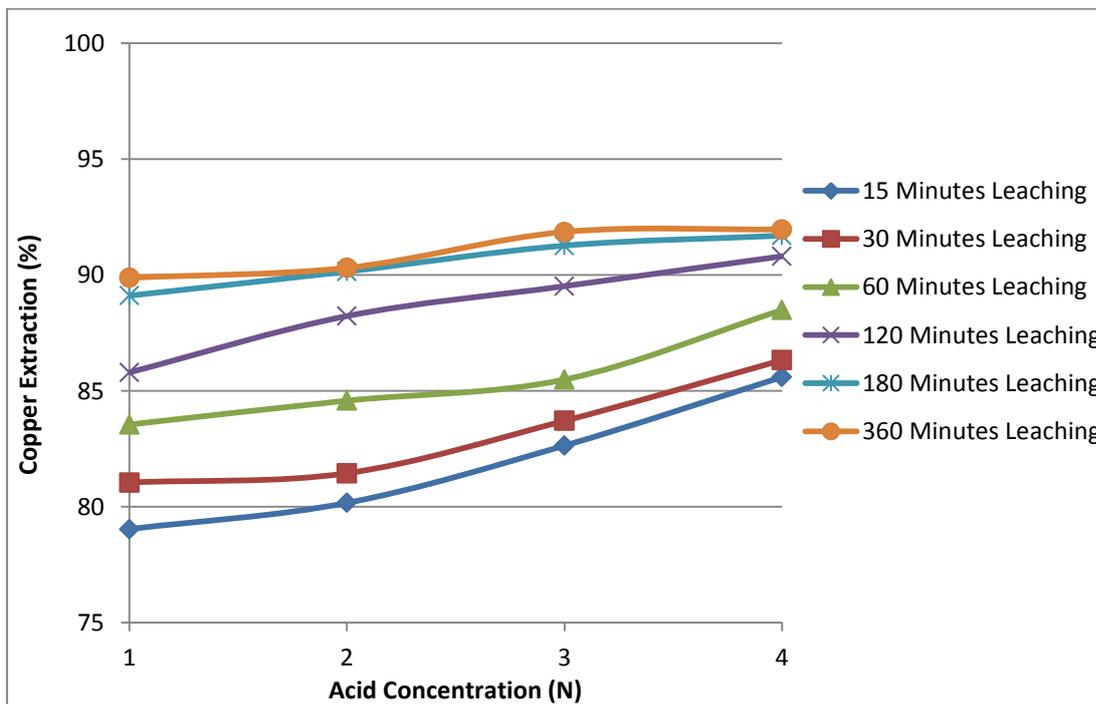


Figure 29: Effect of Sulphuric Acid Concentration on Copper Extraction

The highest copper extractions were obtained in the experiments carried out with 4N acid concentration in all leaching durations. This behavior was expected as higher sulphuric acid concentration used in the experiments resulted in more rapid dissolution of copper from the ore and therefore their more rapid transfer of copper to the pregnant leach solution. Although the highest copper recovery was obtained in the experiments carried out with 4N H₂SO₄ concentration, extraction percentages showed a slight increase above 1N sulphuric acid concentrations for 360 minutes of leaching duration. Therefore following tests were carried out with 1N sulphuric acid concentration.

4.3.4 Effect of Pulp Density

In the study, the effect of pulp density was also investigated. For this purpose; four different solid liquid ratios, namely 1:4 g/cm³, 1:5 g/cm³, 1:6 g/cm³, and 1:8 g/cm³ were used for the experiments. During these tests, weight of sample (50 g), particle size of the sample (100% -250 microns), H₂SO₄ concentration (1N), and leaching temperature (room temperature) were kept constant. The results of the experiments are tabulated in Table 21, and presented in Figures 30, 31, 32, 33, and 34.

Table 21: Extraction of Copper at Different Pulp Densities

Solid Liquid Ratio (g/cm ³)	Leaching Duration (min)	Copper Extraction (%)
1:4	15	77.31
	180	88.07
	360	88.81
1:5	15	79.04
	180	89.11
	360	89.88
1:6	15	80.77
	180	90.05
	360	90.22
1:8	15	80.98
	180	90.72
	360	91.37

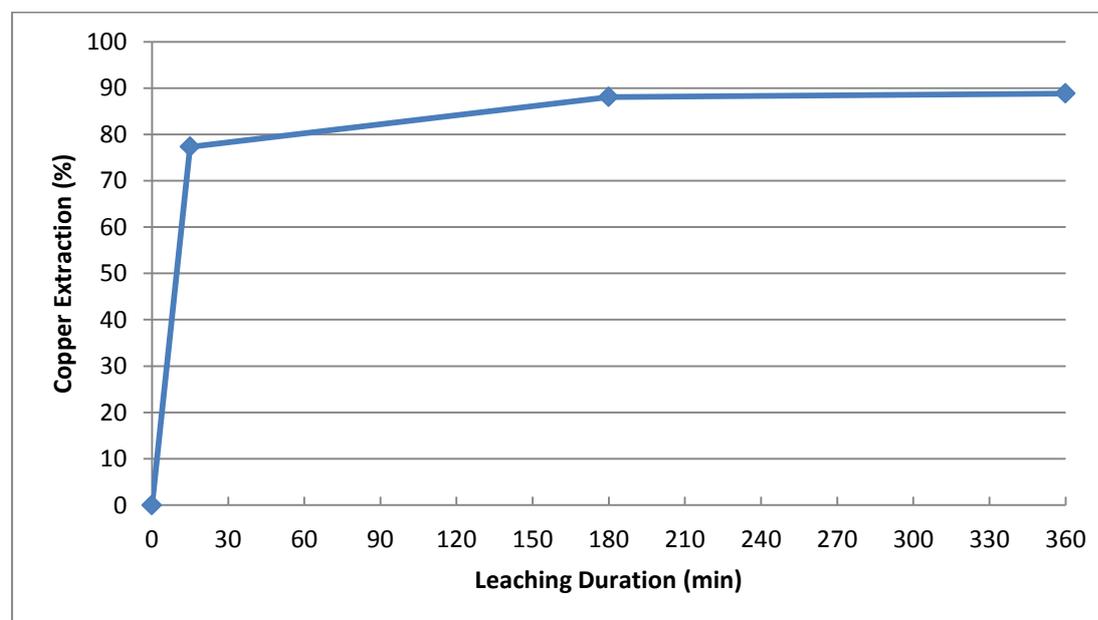


Figure 30: Copper Extraction Percentage at 1:4 g/cm³ Solid Liquid Ratio

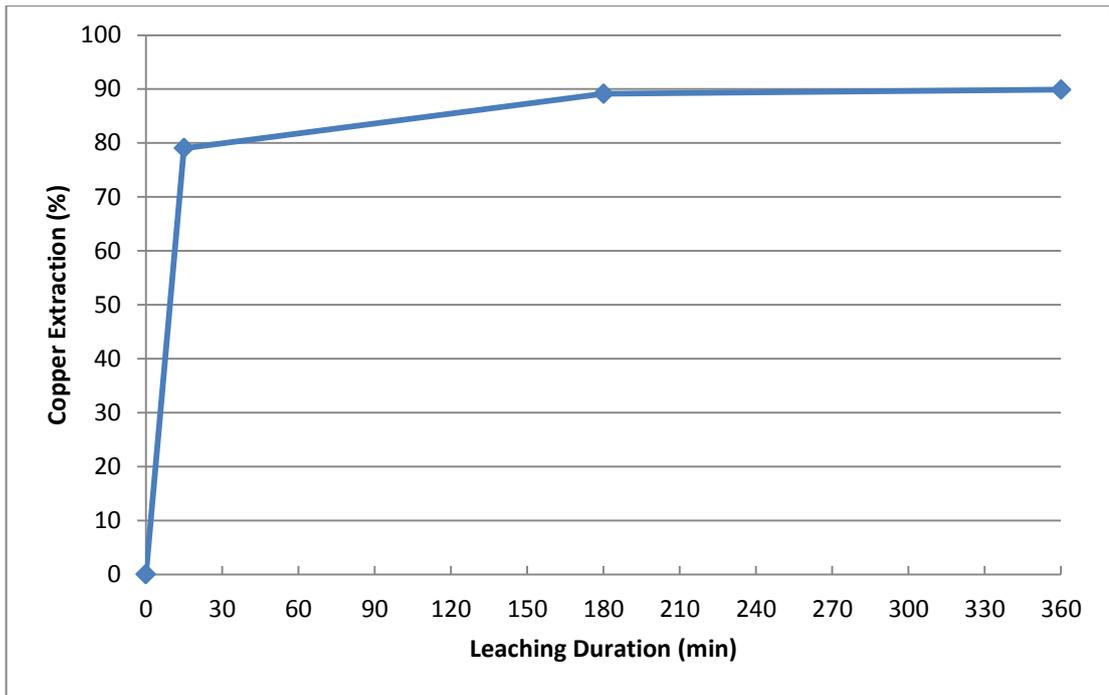


Figure 31: Copper Extraction Percentage at 1:5 g/cm³ Solid Liquid Ratio

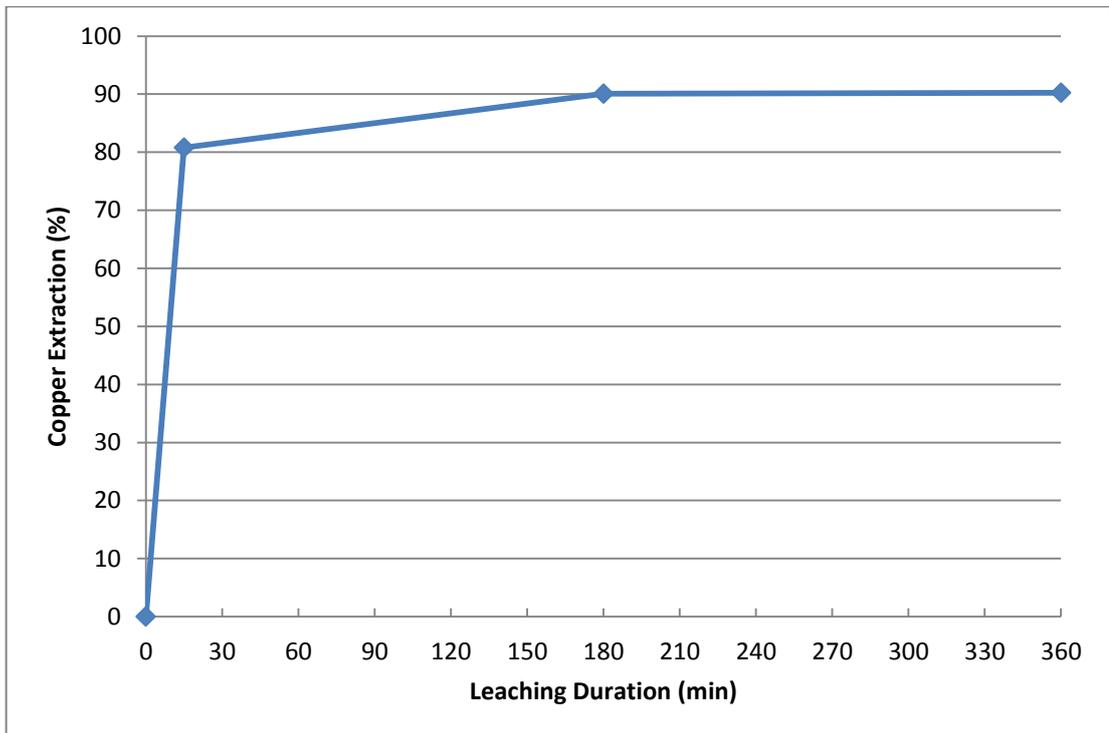


Figure 32: Copper Extraction Percentage at 1:6 g/cm³ Solid Liquid Ratio

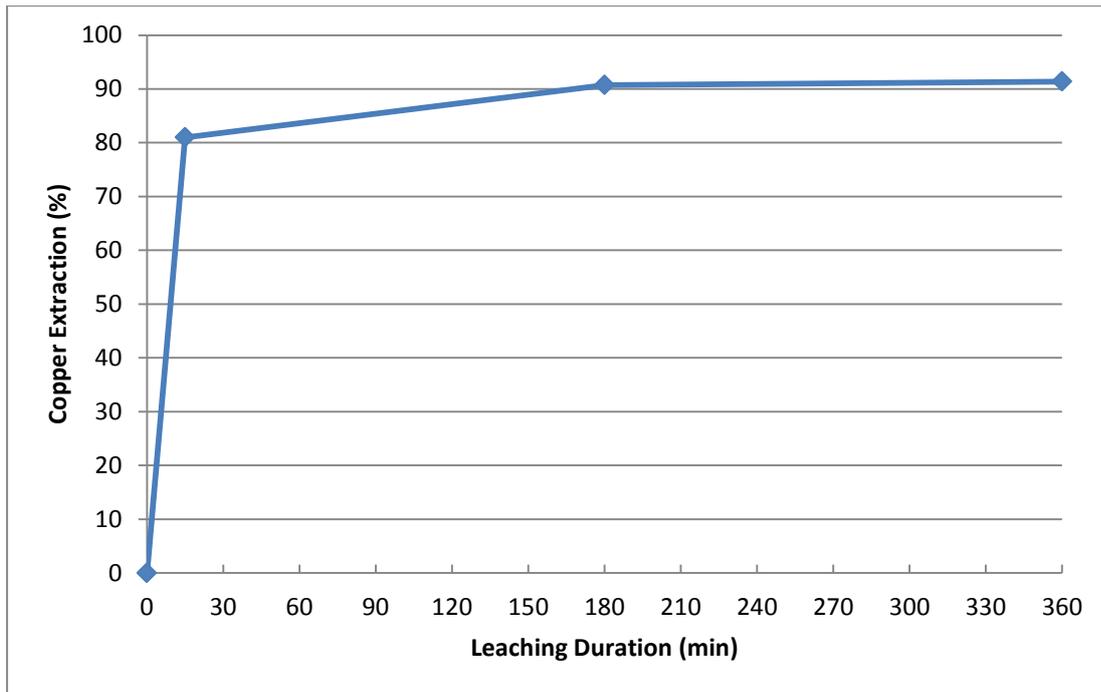


Figure 33: Copper Extraction Percentage at 1:8 g/cm³ Solid Liquid Ratio

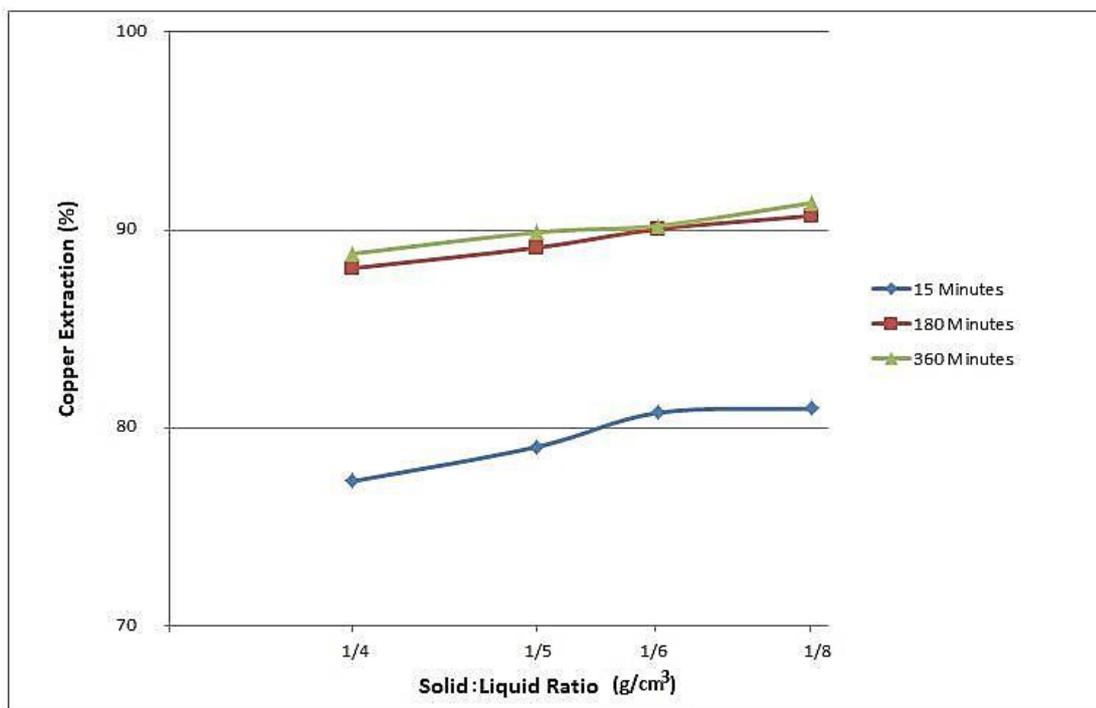


Figure 34: Effect of Solid Liquid Ratio on Copper Extraction

The highest copper extraction percentage values were obtained with the experiments carried out with 1:8 g/cm³ pulp density where viscosity of the pulp is relatively low. Although the highest copper extractions were obtained in the experiments carried out with 1:8 g/cm³ pulp density, extraction values showed a slight increase below 1:5 g/cm³ pulp density.

4.3.5 Leach Residue Characterization

XRD patterns of feed sample and its leach residue obtained under the optimum leaching conditions are given in Figures 35 and 36. The pattern of leach residue showed that calcite peaks could not be identified after leaching process, so it can be said that all calcite minerals in the test sample had been dissolved during leaching process. An increase in the intensity of the quartz peaks was also observed in the pattern of leach residue as expected. This was due to the decrease in the amount of other minerals and high resistance of quartz to sulphuric acid.

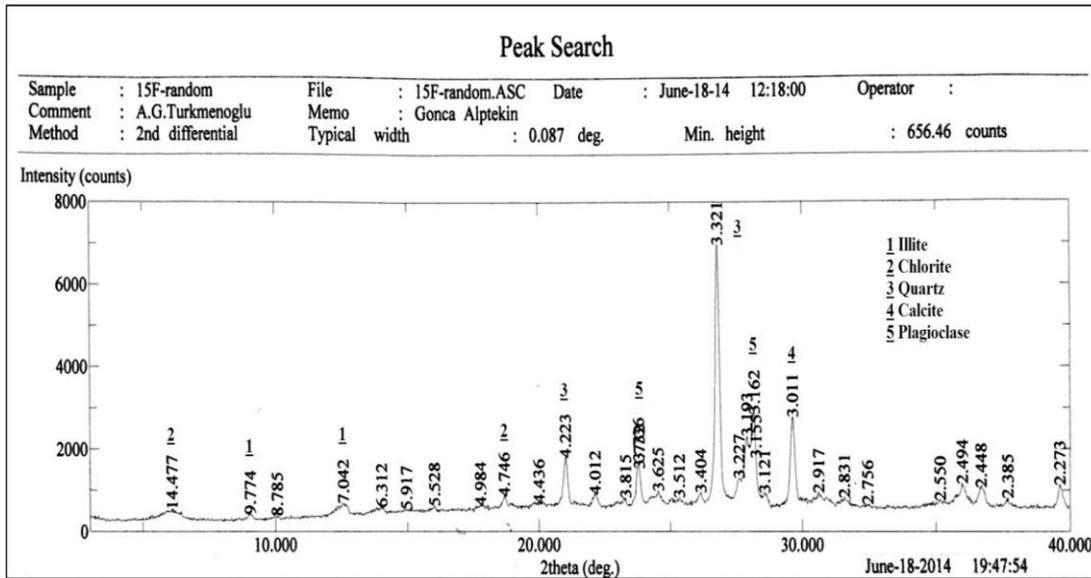


Figure 35: XRD Pattern of Feed

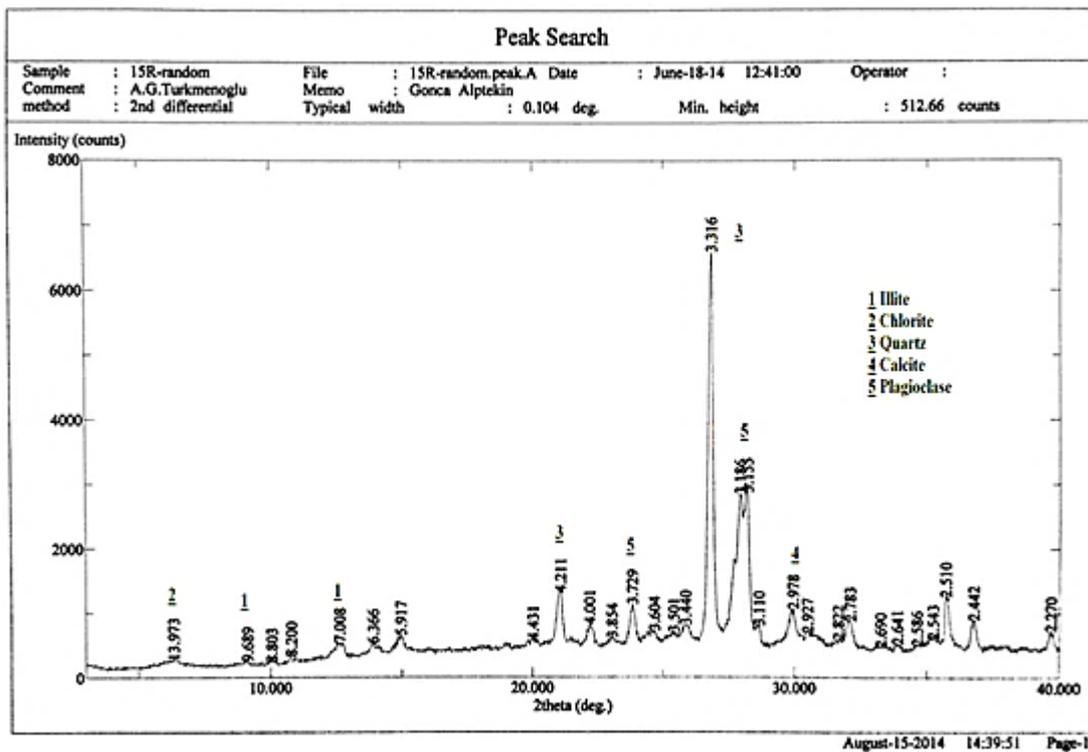


Figure 36: XRD Pattern of Leach Residue

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

In this study, oxide copper from Dangaz region of Çorum was used to investigate the optimum conditions for copper recovery with flotation and agitating sulphuric acid leaching methods. In the light of experimental results, following conclusions can be drawn;

- Native copper (Cu), malachite ($\text{Cu}_2(\text{OH})_2/\text{CO}_3$), cuprite (Cu_2O), and tenorite (CuO), were the main copper minerals in the test sample.
- XRD analysis of the test sample revealed that the major gangue minerals present in the ore were quartz, calcite, illite, chlorite, and plagioclase.
- Flotation test results show that oxide copper ore of Çorum-Dangaz region was not amenable to concentration by flotation. Expected copper concentrate with high grade and recovery could not be obtained with hydroxamate and sulphhydryl type collectors. By using hydroxamate type collector a copper concentrate containing 13.80% Cu was obtained with 57.45% recovery. Use of sulphhydryl type collectors after sulphidisation has resulted a copper concentrate with 34.65% Cu grade and 26.98% copper recovery. Two-stage flotation with hydroxamate and sulphhydryl collectors resulted in a concentrate with 8.69% Cu grade and 61.35% copper recovery. Unsuccessful flotation test results were due to unfavorable morphological properties of native copper for air bubble attachment. Unfavorable flotation characteristics of malachite mineral were the other reason for unsuccessful flotation test results.

- Agitating leaching experiments were conducted with various parameters in order to determine the optimum conditions. It was found that decreasing particle size and pulp density and increasing leaching time acid strength increased copper recovery.

- The optimum conditions for agitating sulphuric acid leaching were 3 hours leaching duration, 1 N sulphuric acid concentration, 100% -250 microns particle size, and 1:6 g/cm³ pulp density. At the optimum leaching conditions, it is seen that 90% copper extraction was possible.

Based on the experienced gained through this thesis, the following recommendation can be given for future extension of the study;

- It is recommended that to increase both grade and recovery of copper concentrate by froth flotation, flotation characteristics of malachite mineral should be studied in detail.

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APPENDICES

A. METU TAP WATER ANALYSES DONE BY ENVIRONMENTAL ENGINEERING DEPARTMENT OF METU

Parameters	Unit	Tap Water in METU Campus
Cr	mg / L	< 0.02
Pb	mg / L	< 0.001
As	µg / L	< 1.0
Se	µg / L	< 1.0
Cd	mg / L	< 0.001
F	mg / L	0.34
Cl	mg / L	54.5
SO ₄	mg / L	147
Fe	mg / L	0.042
Mn	mg / L	< 0.03
Cu	mg / L	< 0.001
Zn	mg / L	0.011
Ag	mg / L	< 0.005
Ca	mg / L	151
Mg	mg / L	26.3