EVALUATION OF KOSOVO-ARTANA CONCENTRATOR TAILINGS

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

EVALUATION OF KOSOVO-ARTANA CONCENTRATOR TAILINGS

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In this study, evaluation of Kosovo-Artana Concentrator tailings with flotation and leaching method is aimed. The minerological analysis of sample showed that sphalerite, galena, chalcopyrite and their oxidised forms are the main ore minerals in the sample, while pyrite, illite, quartz, calcite and gypsum are the gangue minerals. The metal contents of the sample are 1.2% Zn, 0.75% Pb, and 0.06% Cu.

Flotation tests to produce bulk concentrate of copper-lead and lead-zinc were unsatisfactory. The recovery of the zinc with H_2SO_4 leaching were conducted both at room temperature and at elevated temperature. The effects of various parameters such as leaching duration, concentration of H_2SO_4, pulp density and temperature on the zinc metal recovery were examined. The maximum extraction of zinc was 80% and 89% at room temperature and at 80 °C respectively for 120 minutes leaching period.

Keywords: Tailing, Flotation, Concentrates, Leach

ÖZ

KOSOVA-ARTANA KONSANTRE ATIKLARININ DEĞERLENDİRİLMESİ

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Bu çalışmadaki Kosova-Artana konsantratorü artıklarının flotasyon ve liç yöntemleri ile değerlendirilmesi amaçlanmıştır. Numunenin mineralojik analizi, değerli minerallerin, sfalerit, galen, kalkopirit ve bunların oksitlenmiş formlarını, değersiz minerallerin ise pirit, illit, kuvars, kalsit ve alçıtaşı olduğunu göstermiştir. Numune %1.2 Zn, %0.75 Pb ve % 0.06 Cu içermektedir.

Toplu bakır-kurşun ve çinko-kurşun konsantresi üretmeye yönelik flotasyon testleri başarısız olmuştur. Çinko kazanımına yönelik sülfürik asit ile liç testleri hem oda sıcaklığında hem de yüksek sıcaklıklarda gerçekleştirilmiştir. Bu testler sırasında liç süresi, H_2SO_4 konsantrasyonu, pülp yoğunluğu ve sıcaklık gibi çeşitli parametrelerin etkileri araştırılmıştır. Oda sıcaklığında ve 80 °C sıcaklıktaki 120 dakikalık liç süresi sonrasındaki en yüksek çinko kazanım verimleri sırasıyla %80 ve %89 olmuştur.

Anahtar Kelimeler: Atık, Çinko, Flotasyon, Liç.

To My Family

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INTRODUCTION

1.1. General Remarks

Base metals like copper, lead and zinc have been playing important roles in our daily lives for years. Nature is not generous in supply of these metals and the consumption in supply of these metals in different industries is high and increasing rapidly. Therefore, nowadays tailings are retreated to recover the residual metallic values in it.

Standard practice in treating complex copper-lead-zinc ore is selectively depress zinc minerals using cyanides, zinc sulfate, sodium bisulfite and float a copper-lead minerals in bulk concentrate. The copper-lead bulk concentrate is then separated into a copper concentrate and a lead concentrate in a separated circuit. Selectivity against to pyrite is the major problem in flotation of complex sulphide ores. Another problem is the activation of zinc minerals by dissolved copper ions. Oxidation of sulphide minerals is an inevitable phenomenon during the storage of flotation tailings in dump area. This also decreases the selectivity during flotation of valuable ore minerals. Therefore, the flotation of complex sulphide ore tailings is one of the most difficult and complicated concentration task that base metal metallurgist and mineral processing engineer have to solve. Up to present no study for the evaluation of Kosovo-Artana concentrator tailings have been conducted.

1.2. Objective of the Thesis

There are two objectives of this research

1- to find out the optimum flotation conditions for concentration of valuable minerals in tailing.

2- to determine the optimum leaching conditions to extract zinc metal from tailings.

CHAPTER 2

LITERATURE SURVEY

Complex sulphide ores typically containing lead, zinc, copper, precious metals and sulphur, represent considerable reserves and resources in the contained values. Flotation is the only process that enables the separation of the various major mineralogical constituents of a complex sulphide ores. The flotation process is particularly able to make a clean separation with respect to pyrite; however, attaining selectivity between valuable sulphides to obtain selective concentrates with desired purity and high metal recovery has presented difficulties as evidenced by a vast number of literature devoted to the subject. Barbery (1986) concluded that hydrometallurgical processes could be combined with flotation for maximum efficiency in recovering values into concentrates.

Owing the usage of inefficient technologies about a century ago, there accumulated about 1 million tons of gravity and flotation tailings and slags of Balya containing considerable amounts of lead and zinc (Bulut et. al., 1994; Göktepe et al., 2000). The tailings of the zinc flotation stage may contain significant quantities of lead as well as interfering and gangue minerals (undesirable impurities) such as pyrites and silicates. The degree of oxidation in lead ores may range from slight tarnishing of the galena to complete oxidation (Bulut et. al., 1994).

A brief review of the complex sulphide ore processing literature relavant with the scope of this thesis is presented in the following sections.

2.1. Flotation

A prerequisite for the selective seperation of sulphide minerals is to grind complex sulphide ores at their liberation size, which is major achievement in itself. The size at which particles become sufficiently liberated is a function of the physico-chemical conditions prevailing during the ore deposit formation which may have resulted extremely intricate association of the valuable minerals. Therefore, it is of paramount importance to obtain quantative mineralogical information on complex ores before developing a selective flotation sheme.

Another factor of major importance in the perfomance of selective flotation is the surface composition of the sulphide minerals. Sulphide minerals are instable in atmospheric conditions, and considerable changes on their surface occur during their oxidation in flotation systems. In the following series, some of the sulphide minerals are listed in the order of diminshing tendencey toward oxidation (Tolun, 1987).

Arsenopyrite>Pyrite>Chalcopyrite>Sphalerite>Galena>Chalcocite

The most extensively studied sulphides are those of zinc and lead. This is not surprising since these are present in the most common sulphide ores. Zinc sulphide ores are particularly interesting, in that they prove difficult to beneficiate compared to lead sulphide ores in that a metal ion must be added to the suspension to activate the surface to enable the collector to adsorb and the zinc mineral to be converted to a floatable form. Usually Cu^{2+} is added to the pulp to perform this function. Electrokinetic phenomena have been used to eluciadate the differing surface chemical behaviour of these important sulphides.

The studies related to galena were connected with the effect of metal ions on its zeta potential. Sun (1943) described the mechanism of slime coating in terms of electrostatic attractions, and use zeta-potentials to show how their coating depended upon the signs of the adsorbate and adsorbent. Slime coatings were prevented when the zeta-potential of the slime and of the particle were both high and of the same sign. Moreover, Neville and Hunter (1976) found that it is a very distinct effect on the value and sign of zeta-potential. The iep of their galena sample varies between pH 2 and pH 4 depending upon equilibration conditions. At low pH conditioning they observed negative to positive and positive to negative charge reversals at pH 6 to pH 1, characteristic of hydroxide or basic sulphate precipitation on the PbS surface.

The difficult complex sulphide ores are usually zinc rich with secondary lead and tertiary copper. Botcharov et al. (1975) concluded that, in the selective flotation of copper-zinc-pyrite ores, selectivity between copper and zinc minerals depends on the percentage ratio of copper and zinc content, and considered ores with Cu:Zn ratios below 1.5:1 as comparatively easier to concentrate.

2.1.1. Depression of Pyrite

The selective depression of pyrite depends on the mineralogical composition of the ore, liberation size, degree of oxidation, transformation to variable Fe:S compounds, types of ore minerals to be recovered (Cu, Pb, Zn), presence of secondary minerals in the ore, the surface conditions of the minerals in the ore, and presence of the slimes and carbonaceous material.

Pyrite depression methods is explained below sections.

a) Lime depression:

The depression of pyrite by lime is the result of an increased concentration of hydroxyl ions and the specific effect of calcium or carbonate-bicarbonate ions on pyrite (Roger, 1962). Hu(1985) concluded that it is advantageous to add lime in ball mill because lime dissolves in water to form $Ca(OH)_2$ which dissociates to Ca^{2+} and OH^- ions. In grinding OH^- ions react with copper ions to form basic copper salts or copper hydroxide precipates. At the same time, other metallic ions such as Fe will be precipated, too. Thus, activation of pyrite and sphalerite by copper ions can be reduced. In the mean time, OH ions may react with the iron ions on the surface of pyrite to form $Fe(OH)_3$ and $Fe(OH)_2$ precipitates leading to hydrophillic pyrite surface.

b) Lime-Cyanide depression:

This method has been successfully studied and used (Sutherland and Wark, 1953; Rogers, 1962). This depressant combination is effective for finely disseminated pyritic ores in the pH range of 11 to 11.5, and is not effective for the depression of pyrite in oxidized ores.

c) Lime-Cyanide-Sulphurous acid depression:

This combination of reagent is used to depress pyrite from partially oxidized lead-zinc, copper-lead-zinc, and copper-zinc ores (Bulatovic and Wyslouzil, 1983). The points of lime, cyanide and SO_2 addition, and pH values are critical when using this combination. The depression of pyrite improves at pH values higher than 8.

d) Zinc-Cyanide complexes:

Zinc sulphate and cyanide are poor pyrite depressants for pyrite or marcasite (Bulatovic and Wyslouzil, 1983).

e) Depression of pyrite by oxidation:

Air or such oxidants as $KMnO_4$ and $Na_2Cr_2O_7$ can successfully depress pyrite (Bulatovic et al., 1965; Plante et al., 1963). Aeration is widely used for ecomonomic reasons and better results but oxidants are avoided because they also have a strong depressing effect on other sulphides. Ergunalp and Weber (1985) applied aeration to massive sulphides and depressed pyrite successfully.

f) Depression by Na_2SO_3 and $Na_2S_2O_{5:}$

Roberts et al. (1980) suggested the use of Na_2SO_3 and $Na_2S_2O_5$ in combination with lime at pH 10 to 11 to depress pyrite.

i) Depression of organic mixtures:

Bulatovic and Wyslouzil (1982) applied mixtures of starch, dextrin, quebracho, lignin sulphonates and inorganic depressants such as NaCN, $ZnSO_4$ and Na_2S to depress pyrite, pyrrhotite and arsenopyrite.

2.1.2. Depression with Sphalerite

The reagents that are most commonly used in depression of sphalerite are the mixtures of the zinc sulphate with alkalis such as Na_2CO_3, KCN, Na_2SO_3 and lime. The choice of modifiers differs from the ore to ore, and the development and control of processes is generally difficult matter. Selective depression of sphalerite by these zinc-containing reagents with respect to galena, pyrite, or chalcopyrite is due to the formation of deposits of hydrophilic zinc complex species at the surface of the sphalerite such as $Zn(CN)_2$, $Zn(OH)_2$, $ZnCO_3$.

The effectiveness of the cyanide species increased in order $CN^- < Zn(CN)_2 < Zn(CN)_3^- \approx Zn(CN)_4^{2-}$ and that the interaction of the surface with such reagents results in the formation of a film of a hydrophilic zinc species that prevents reaction with xhanthate.

Solozhenkin and Vasyukevitch (1958) investigated the depressing action of zinc sulfate and zinc cyanide compounds and complexes. They found that considerable adsorption took place from zinc sulfate solutions and that this adsorption was irreversible. Moreover, the depression of sphelarite is caused by $Zn(CN)_2$ or at higher alkalinities, $Zn(OH)_2$, and that soluble species such as $Zn(CN)_4^{2-}$ merely act as a source of $Zn(CN)_2$ or $Zn(OH)_2$ (Finkelstein and Allison, 1976).

Sphalerite depresses at high pH values in $ZnSO_4/Na_2CO_3$ solutions. Grosman and Khadshiev (1966a, 1966b) showed that the sphalerite was depressed in $ZnSO_4/Na_2CO_3$ solutions at higher pH values greater than about 6, and that the floatabilities of pyrite, chalcopyrite and galena were much less affected.

Depression of sphalerite by reagents containing zinc salts is due to the formation of deposits of hydorphilic zinc complex species at the surface of the sphalerite. These species are similar to, if not identical with, bulk precipitates such as $Zn(CN)_2$, $Zn(OH)_2$, $ZnCO_3$, and basic zinc carbonates and sulfates. Relatively thick films are required for effective depression of sphalerite.

2.1.3. Activation of Sphalerite

Sphalerite does not float in alkali medium with xanthate. Activation by adding heavy metal cations such as Cu^{2+}, Pb^{2+}, Sb^{2+}, Cd^{2+} are needed for the flotation of sphalerite. The most commonly used activator is copper sulphate. The sphalerite will float readily over a wide range of pH values with small dosages of xhantates after addition of copper sulfide. It is much less soluble than zinc sulphide and addition of copper ions to sphlalerite changes the surface to form an insoluble copper sulphide.

Steiniger (1968) treated the mineral with copper ions and xanthate simultaneously, and floated it immediately afterwards. The good recoveries were obtained at pH values greater than 9 and less than a value that varied from about 8 to 5.5 as the dosage of $CuSO_4$ increased.

Holmsen (1966) observed that copper adsorption on sphalerite was strongly dependent on pH, and decreased rapidly at high pH values. Bushell et al. (1961) found that pH should not exceed 11.2 for copper activation of sphalerite for sphalerite-pyrrhotite ore, and 12.2 for a sphalerite-pyrite ore.

The activation reaction of sphalerite is effectively ion exchange between copper and zinc. The mechanism probably involves the first simple lattice replacement reaction, or a dissolution/precipitation reaction, and then a lattice rearrangement.

2.2. Zinc Leaching

Zinc production can be achievable by hydrometallurgical and pyrometallurgical process. Zinc concentrate from its sulphide ores can be processed by hydrometallurgical and pyrometallurgical process which are common zinc production processes.

New developments in acid leaching and solvent extraction to allow the zinc source processing, expect of sulphide zinc ores, such as low grade zinc ores and electric arc furnace dust (Basir and Rabah, 1999; Leclerc and et. al., 2003; Canbazoğlu et al., 2009., Souza et al., 2007). The leaching is the first and the most important step of producing metal economically by using hydrometallurgical process (Abdel-Aal., 2000).

Research shows that sulphuric acid leaching of zinc oxide dissolves zinc minerals with high recovery. Abdel-Aal, 2000 dissolved %94 of zinc from a low grade silicate ore with 180 minutes leaching time and 70 °C. Moreover, Longova (2009) achieved HCl microwave laching of zinc ferrites. NH_4Cl leaching of smithsonite and sulphuric acid leaching of low grade oxide ores zinc mineral in column conditions was determined (Wen-ging et al., 2007). Canbazoğlu and his colleques (2009) studied sulphuric acid leaching parameters as selectivity, chemistry and kinetics of dissolutions of zinc and other metals from low grade oxide ores.

Lead containing wastes have been subjected to various recovery methods. Brine leaching one of the method which is widely used for recovery of lead mineral (Abdollahi et al., 2006; Raghavan et al., 1998). Brine leaching is based on the formation of complex chlorides of lead in concentrated chloride solutions (Cöcen et al., 2010). Lead sulfate is soluble in saturated chloride solutions which is acidified by HCl, H_2SO_4 or chlorine water, but it is insoluble in water (Habashi, 1969.)

2.3. Previous Flotation Studies on Tailings

The tailing deposit near Balya, Balıkesir, Turkey was remined between 1880 and 1935 by French company. The lead-zinc tailing deposit has about 1 million tons of flotation tailing and slags including considerable amount of zinc and lead. The tailing deposit contains 3.12% Zn, 3.43 %Pb, 0.71

g/ton Au and 74 g/ton Ag which are suitable grades for flotation (Önal et al., 2010).

The flotation was conducted with sulfide flotation which was found to be effective for high zinc content for bulk concentrate, however; oxide flotation was necessary to obtain high lead content. The important part of lead in galena was partly oxidized and tarnished, therefore, sodium sulfide or sodium hydrosulfide was added in the concentrates (Önal et al., 2010).

The first test was conducted as three rougher Pb-Zn flotation stages followed by two cleaning stages. The pyrite in the concentrate was depressed by adding 1000g/ton $CuSO_4$, 150 g/ton Aerophine 3418A was used as collector and MIBC as a frother was added 30g/ton in rougher stage. While oxide and sulfide minerals were floated together in first rougher stage, in second stage 600 g/ton Na_2S (sodium sulfide) was added as sulfidizing agent. Aero 407 and KAX were added 150 g/ton each in rougher concentrate. However, in bulk rougher concentration stage, obtained concentrates were not marketable (Önal et al., 2010).

In the second test, Pb-Zn bulk flotation were tried by applying number of roughing and cleaning stages. Moreover, because of the high oxidized lead content, oxide flotation were conducted as four rougher flotation stages. The reagents used in rougher flotation were 2000 g/ton $Na_2S_2O_5$, 1000 g/ton $CuSO_4$, 225 g/ton Aero 3418A and 12.5 g/ton MIBC, however; 200 g/ton $Na_2S_2O_5$ were added in cleaning stages. In oxide flotation, 2000 g/ton Na_2S, 200 g/ton KAX and 200 g/ton Aero 407 which was used as promoter in combination with isopropyl or amyl xanthate as collectors. The recoveries of the floation tests were 12.5% Pb and 43.02 % Zn, on the other hand; most of the Zn remained in the tailings (Önal et al., 2010).

Önal and co-workers (2005) used Aerophine 3418A as a collector, $Na_2S_2O_5$ as a depressant for pyrite and $CuSO_4$ as an activator at rougher stages. The produced concentrate with 43.02% Zn and 12.5% Pb were marketable.

Ball and Rickard (1976) studied lead-zinc-copper concentrator plant tailings in Southeast Missouri. The concentrator had a capacity of 4,200 tpd. The bulk concentrate was cleaned once or twice, depending on the quantity. The cleaner tails and scavenger concentrate were returned to the distributor of the rougher circuits.

The cleaned bulk concentrate were the feed to the separation circuit. They were treated with sulfur dioxide and starch to depress the galena, and the chalcopyrite were floated in four cells. The underflow from these cells was the final lead concentrate and was pumped to the lead thickener. When the lead to zinc ratio was high, the froth product joins the copper-lead scavenger concentrate; when the ratio was low, copper sulfate was added and a zinc rougher concentrate was produced.

In lead-copper circuit, the first operation was to recover all of the lead and copper minerals possible while depressing zinc and iron sulfides and the gangue minerals. The chalcopyrite was difficult to float until the original grains were broken. Sulfur dioxide or sodium bisulfite were the only reagents so far found that activate these chalcopyrite grains, but the large quantity required damages the galena flotation so much that their use was not practical. Because of the its poor flotation characteristics, the chalcopyrite tended to depress in the lead-copper cleanars. Therefore, enough sulfur dioxide was fed to the lead-copper cleaners to activate the chalcopyrite. Moreover, very small quantities of cyanide were fed to the rod mills for iron and zinc depression. The poor flotation properties of the galena and chalcopyrite required a powerful sulfide collector. Amyl xanthate, either the potassium or sodium salt, were the most effective in the process. Dowfroth 250 was the principal frother. When the froth was too tough or persistent, MIBC was substituted for a portion of the Dowfroth. Lime was used for pH control. The maximum floataion rate in the lead-copper circuit was pH 8.5 to 9.0. In the bulk Pb-Cu concentrate, Pb and Cu recoveries were74% and 30%, respectively.

In zinc ciruit, the tailings from the copper-lead bulk float were activated with copper sulfate and the sphalerite recovered. Lime was used to maintain pH of 11.0 to 11.5 in the cleaners and 9.0 to 9.5 in the roughers. Cyanide was fed to the zinc cleaners because the iron and zinc minerals were very sensitive to cyanide. About 20% of the total cyanide used went to the zinc cleaners to maintain concentrate grades.

Hayashi et al. (1979) studied Çayeli black ore by using sulphur dioxide at high temperature. They achieved copper concentrate containing 23.77 % Cu and 3.57% Zn and zinc concentrate containing 45.3% Zn and 3.38% Cu. In Cu circuit, lime was used to maintain pH in 6.5. The collector was selected as Aerofloat 208 which was put 50 g/ton in Cu rougher. Dowfroth 250 was choosen as frother and the total amount of it was 10 g/ton in rougher. The tailing from the copper bulk float were activated with 200 g/ton $CuSO_4$. The pH in the cleaners were arranged as 11.5. The recoveries were 90% and 70.4% for copper and zinc, respectively.

2.4. Plant Practice and Laboratory Studies of Leaching

The the tailing sample containing 10.08% Zn, was obtained from Aladağ, Kayseri. The sample had very fine particle size which was 76.85% of -45 micron. H_2SO_4 acid was used in the leaching experiment with different consumptions.

The leaching conditions were determined as 50 g of tailing sample, 400 ml leach volume and 125 g H_2SO_4/L of acid concentration. According to leach parameters, the leach time was observed regarding of the zinc recoveries which were obtained during the leaching. Zinc recovery was achieved 86.26% after five minutes and the increased in recovery to 89.56% was observed after 45 minutes. Due to the secondary reactions in leaching medium after 120 minutes, the recovery of Zn was observed to decrease. Therefore, optimum leaching time was determined as 60 minutes (Canbazoğlu, Ö., et.al., 2010).

The leaching temperature was determined by keeping constant the other leaching parameters. Tempretures of 40, 60, 80 °C were tested in the experiments. Weight loss increased to 16.37% to 30.17 while the temperature was raised to 40 °C to 80 °C, respectively (Canbazoğlu, Ö., et.al., 2010). Therefore, optimum temperature was considered as 60 °C which had the optimum weight loss percent of 19.32 and acid consumption of 629 kg/ton.

Acid concentration another factor was to be considered in the studies. The concentrations from 38 g H_2SO_4/L to 125 H_2SO_4/L were tested, the weight loss percent and acid consumption parameters were followed during experiments to determine optimum acid concentration(Canbazoğlu, Ö., et.al., 2010). Consequently, 100 g/L acid consumption were determined in order not to change the other parameters such as 60 °C of leaching temperature, tailing sample amount of 100 g, 800 ml leach volume and 60 minutes leaching time.

Aladağ tailings leach experiments showed that the recoveries were achieved 89.54% Zn and 19.00% Fe were extracted by consuming 565 kg/ton acid with 60°C of leaching temperature and 100 g/L acid concentration (Canbazoğlu, Ö., et.al., 2010).

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURES

3.1. Materials

The test samples used throughout the study were obtained from tailings dump of Kosovo Artana, by the help of drillholes. Due to high moisture content, collected sample was first dried at open atmosphere in the mineral processing laboratory of Mining Engineering Department of METU. Then, by coning and quartering and riffling represantative test samples were prepared.

3.1.1 Chemical Composition

The complete chemical analysis of test sample was carried out by using XRF analyzer. The result of analysis is given in Table 1. The Zn, Pb, and Cu content of representative sample were found as 1.17%, 0.76% and 0.06% respectively.

Table 1. Chemical Composition of Test Sample.

Component	%
Zn	1.17
Pb	0.76
Cu	0.06
Fe	29.6
Si	7.43
Al	1.63
Mg	0.27
Ca	5.09
S	28.16

3.1.2. Particle Size Analysis

In order to determine the particle size distribution of the ore, wet sieve analysis was carried out. Pb, Zn, and Cu analyses of each size fraction were performed by Karadeniz Holding by using XRF analyzer. The results of these analyses are given in Table 2.

Table 2. Wet Sieve Analysis Results and Zn, Pb and Cu and Distribution of the Sample.

Fractions	**Weight**	**Zn**		**Pb**		**Cu**	
(µm)	**(%)**	**Grade (%)**	**Dist.(%)**	**Grade (%)**	**Dist.(%)**	**Grade (%)**	**Dist.(%)**
+150	11.50	1.44	13.35	0.37	5.99	0.03	5.75
-150+75	4.06	1.25	4.09	0.17	0.97	0.06	4.05
-75+45	11.07	1.17	10.44	0.25	3.90	0.04	7.36
-45+38	11.57	1.01	9.42	0.25	4.07	0.04	7.70
-38	61.80	1.25	62.70	0.98	85.07	0.07	75.14
Calculated Total	100.00	1.24	100.00	0.71	100.00	0.06	100.00

According to the wet sieve analysis of the sample, as it is seen in Table 1, 61.80% of the test sample by weight is under 38 micron, and important portion of zinc, lead and copper metals are collected in this size fraction.

3.1.3 Mineralogical Analysis

To obtain information about the mineralogical composition of the sample X-Ray diffraction (XRD) analysis and optical microscope examinations were carried out. The dominant major sulphide detected by XRD is pyrite. Sphalerite, chalcopyrite, galena and their oxidised mineral forms could only optically observed. Quartz, illite, goethite, gypsum, siderite and calcite were the other minerals in the test sample. Minor amount of limonite mineral was observed as a secondary mineral. For mineralogical analysis of the test sample, polished sections were prepared and examined by optical microscope. Both liberated and interlocked pyrite minerals were observed and pyrite was the dominant mineral in the interlocked particles. Sphalerite was observed in minor amount. Some of the sphalerite grains were observed as free particles. However, interlocked sphalerite with pyrite and chalcopyrite having size below 25 microns was dominant. Major portion of galena minerals were found as interlocked form with sphalerite and gangue minerals. Minor amount of free galena was also observed. Chalcopyrite minerals were very finely disseminated in sphalerite grains and pyrite grains and there were also 3-5 µm size chalcopyrite mineral enclosed in pyrite particle.

Figure 1, 2, 3, and 4 show some characteristic micrographs of polished sections.

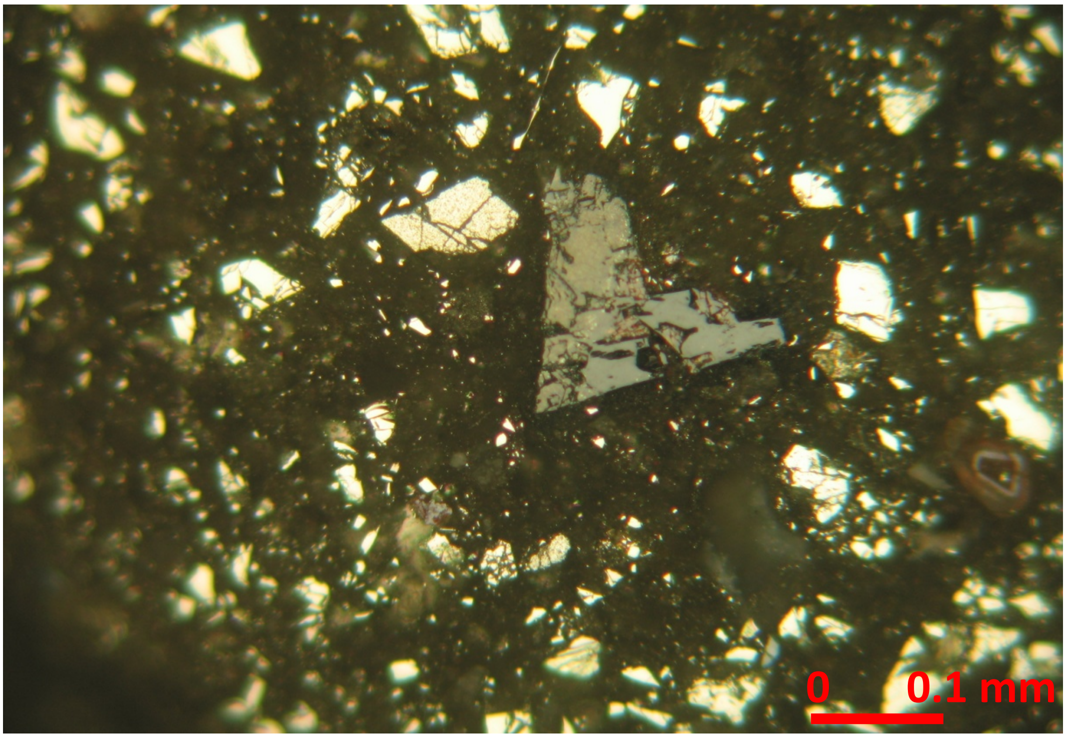


Figure 1. Free sphalerite particle, and give chalcopyrite inclusions in the sphalerite grain, liberated pyrite grains and limonite.

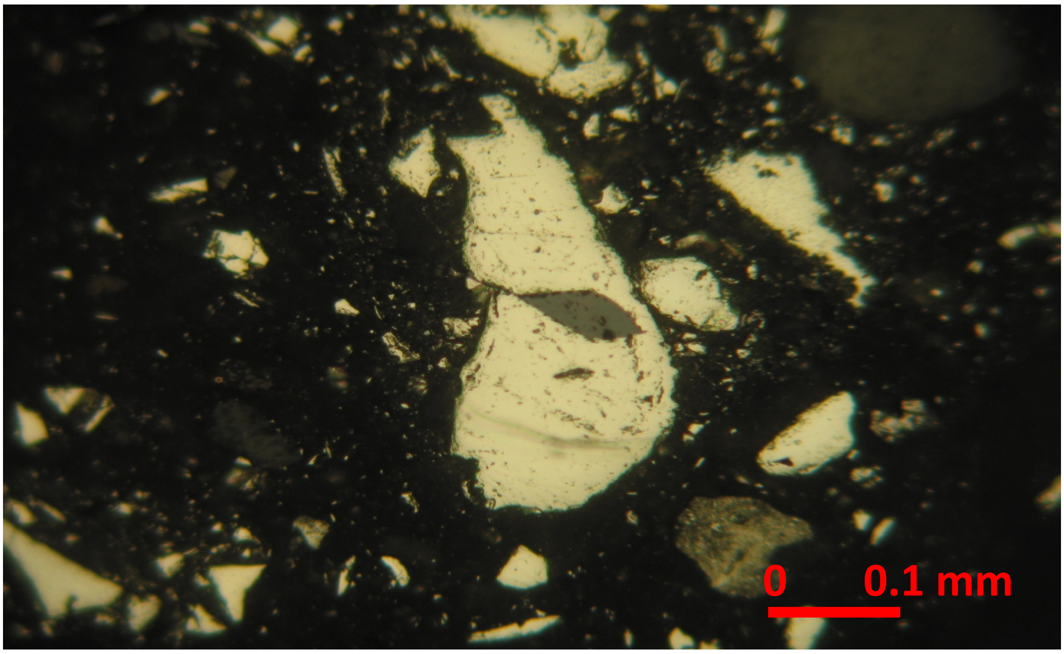


Figure 2. Interlocked sphalerite-pyrite grain and free pyrite particle.

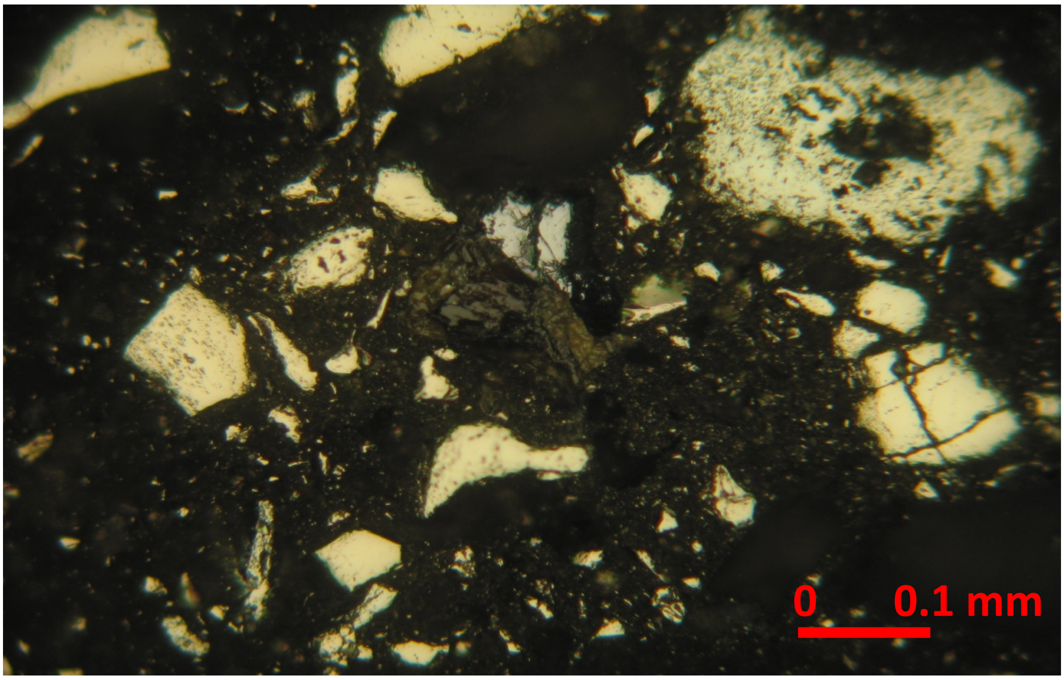


Figure 3. Interlocked sphalerite-galena particles and free pyrite and marcasite particles.

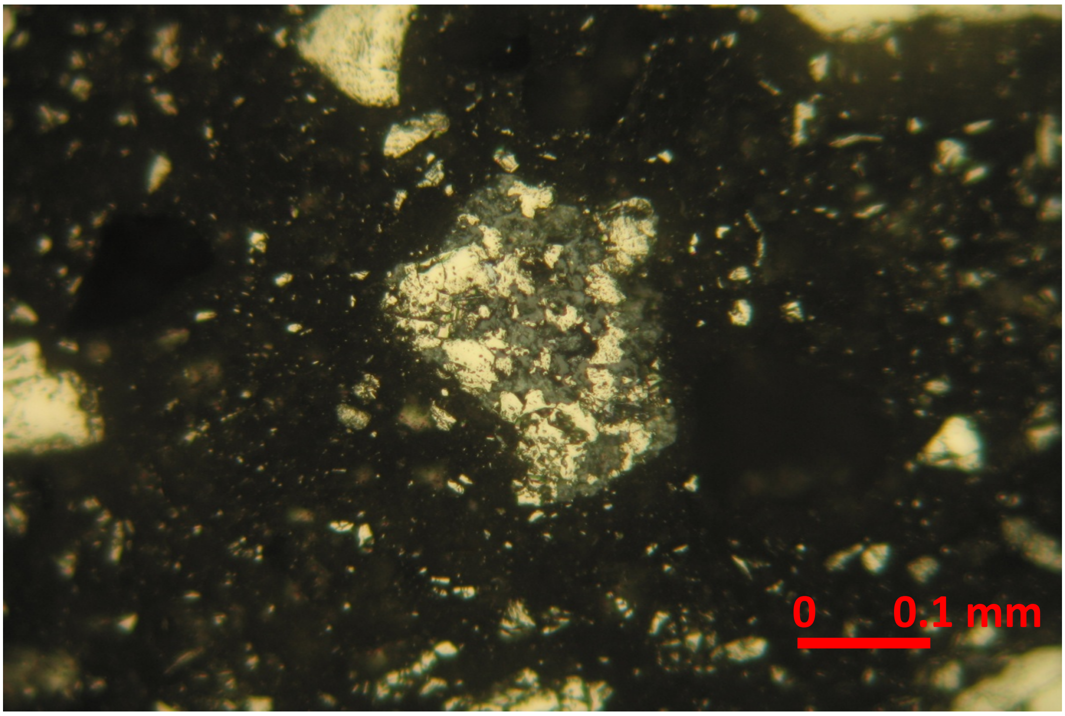


Figure 4. Interlocked pyrite-sphalerite, and very fine free pyrite particles.

3.2 Methods

During the evaluation of test samples two distinct concentration procedures were followed, namely, flotation and leaching.

3.2.1 Flotation Studies

To determine the viability of the tailings to concentration by flotation tests two different flotation schemes were followed. The followed flowsheets are given in Figure 5 and 6.

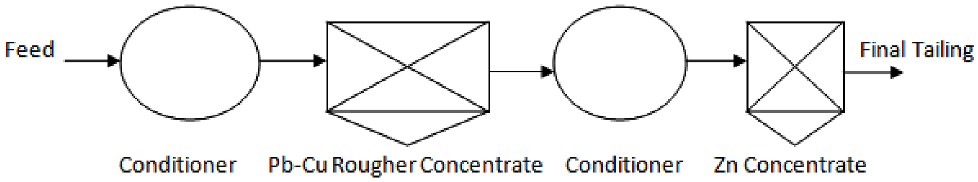


Figure 5. Pb-Cu Bulk Flotation and Selective Zinc Concentrate

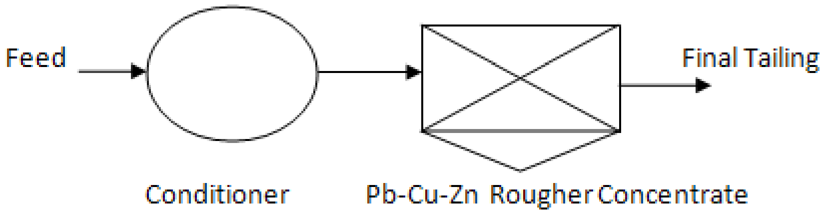


Figure 6. Pb-Zn-Cu Bulk Flotation

During the flotation tests 300 gram of sample and 1 liter volume flotation cell was used. A series of tests were carried out to examine the effects of flotation parameters.

3.2.2. Leaching Studies

Agitative H_2SO_4 acid leaching tests at room and elevated temperature were carried out for the extraction of zinc. During the tests the effects of leaching parameters were examined.

Agitative leaching experiments were carried out with the set up shown in Figure 7. Prepared acid solution of known volume and concentration was placed into the beaker. 25 gram of representative sample was poured into beaker and stirred at a constant speed by a magnet to obtain sufficient mixing at desired time period. At the end of tests, the leached sample was filtered and washed with distilled water. Leach residue was dried at 105 °C, then weighed and analyzed by XRF analyzer. The flowsheet of leaching experiment is shown in Figure 8. Based on residue analysis, the extraction % of Zn were calculated by using the formula given below.

$$\text{Extraction of Zn}(\%) = \left[100 - \frac{(\text{Zn\% in residue x weight of residue})}{(\text{Zn\% in feed sample x weight of sample})}\right]$$

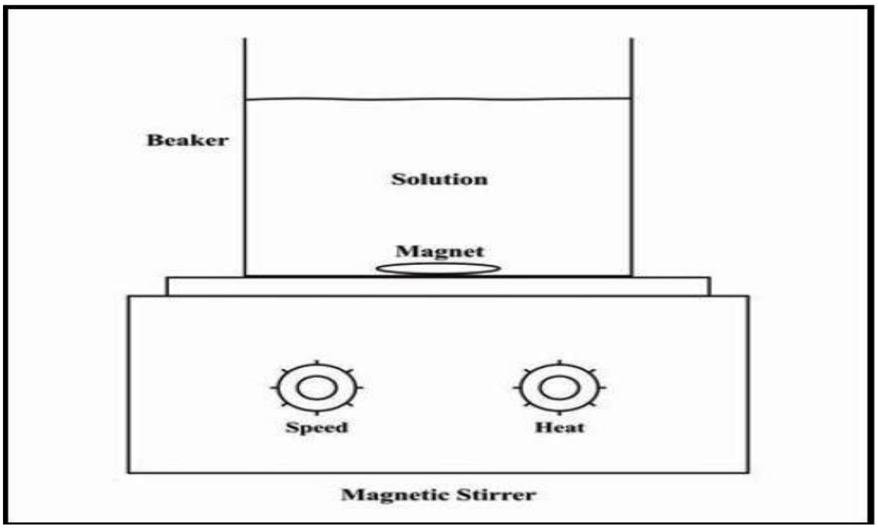


Figure 7. Agitative Leaching Set-up.

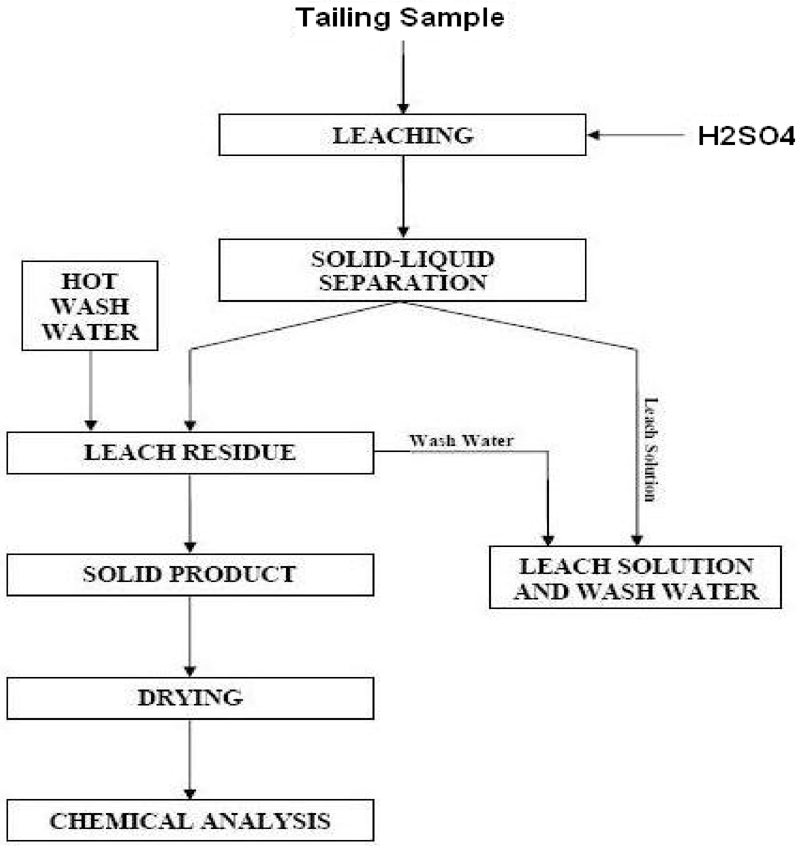


Figure 8. Flowsheet of the Experimental Procedure for Leaching Test

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Flotation Studies

Two fundamentally different flotation schemes were followed.
i- Bulk Flotation of lead-copper minerals.
ii- Bulk Flotation of zinc-lead-copper minerals.

4.1.1. Production of Lead-Copper Bulk Concentrate

Number of flotation tests were carried out to produce bulk concentrate of lead and copper. During these tests lime is used as depressant for pyrite and $ZnSO_4$ is used as depressant for sphalerite, and sulphidizing agent is used for activation of oxidized minerals.

4.1.1.1. Effect of pH Level

Experiments were conducted to determine the floatability of galena and chalcopyrite as a function of pH in the absence of depressant. The lime (CaO) was used to increase pH and depression of pyrite during the flotation. Aerofloat 3418A was used as collector and MIBC was frother of the flotation. The test results are tabulated in Table 3.

Table 3. Effect of pH Level in Cu-Pb Froth Product.

pH Level	Cu-Pb Froth Product						
	Weight (%)	Grade			Recovery		
		Pb %	Cu %	Zn %	Pb%	Cu%	Zn%
10.5	25.61	1.02	1.20	0.07	35.82	25.19	33.86
11	28.17	0.85	1.02	0.07	31.83	26.19	37.66
11.5	25.85	1.05	1.12	0.08	38.17	28.35	37.82
Flotation Conditions Conditioning Time: 5 minutes Frother MIBC: 30 g/ton Collector Amount: 30 g/ton							

Flotation experiments were indicated that, in the absence of the any depressant, Pb-Cu bulk recoveries was not affected by medium pH significantly. Therefore, the furher experiments were carried out by arranging pH level as 11 to be sure about the depression of pyrite.

4.1.1.2 Effect of Collector Type

Flotation depends on the formation of hydrophobic surface. In the case of sulphide minerals, this surface state usually arises through interaction with sulphydryl type collectors. The effect of the collector type was examined using the Aerophine 3418 A, Aerofloat 242, Aero 5415 and Aero 5500 as collector.

Aerophine 3418 A P-based sulfide collector. It was originally developed for the flotation of copper and activated zinc minerals. Figure 9 shows the chemical formula of Aerophine 3418A.

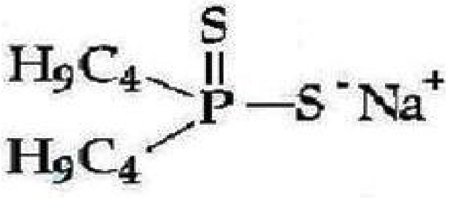


Figure 9. Formula of Aerophine 3418A Collector.

Aerofloat 238 is a R=sec. Butyl. Widely used in Cu flotation and for increasing by-product Au recovery. It combines collecting power with selectivity against iron sulfides. Figure 9, also, shows the general chemical formula of Aerofloat 238 which is Dialkyl Dithiophosphate.

Aerofloat 242 is widely used for flotation of Pb from Pb/Zn ores and Cu/Pb from Cu/Pb/Zn ores. The chemical formula of the collector is Diaryl Dithiophosphate. Figure 10 indicates the chemical formula of Aerofloat 242.

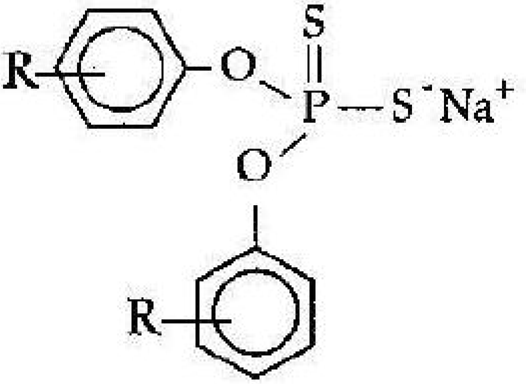
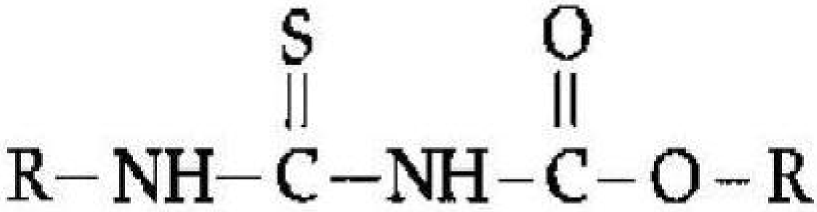


Figure 10. Formula of Aerofloat 242 Collector.

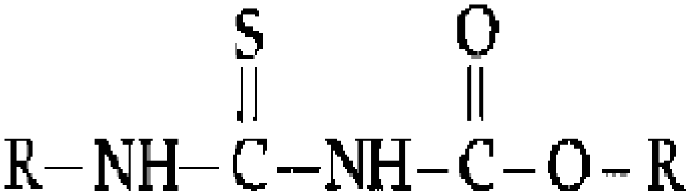
Aero 5415 combines the selectivity of the dialkyl thionocarbamates and the collecting power of xanthates. Moreover, it allows selective flotation of copper ores containing iron sulfides under mildly alkaline conditions (pH 8-10) in contrast to the higher pH values required to depress pyrite when using xanthate and other collectors. The chemical formula of the collector is shown in Figure 11.



$$R-NH-\overset{\overset{S}{\|}}{C}-NH-\overset{\overset{O}{\|}}{C}-O-R$$

Figure 11. Formula of Aero 5415 Collector.

Aero 5500 is functionalized thiourea-based oily collector, is a collector for copper minerals, especially chalcopyrite. It is also a good collector for metallic gold and silver. The chemical formula of the collector is Alkyl Alkoxycarbonyl Thionocarbamate. Figure 12 shows the chemical formula of Aero 5500 collector.



$$R-NH-\overset{\overset{S}{\|}}{C}-NH-\overset{\overset{O}{\|}}{C}-O-R$$

Figure 12. Formula of Aero 5500 collector.

All these collectors are selective for the ores which contain slightly oxidized or easily tarnished copper and lead minerals with high pyrite, pyrrhotite and marcasite content. The test results are tabulated in Table 4.

Table 4. Effect of Collector Type in Cu-Pb Bulk Flotation

Collector Type	Cu-Pb Froth Product						
		Grade			Recovery		
	Weight (%)	Pb %	Cu %	Zn %	Pb%	Cu%	Zn%
3418 A	25.50	1.02	0.07	1.25	34.22	29.75	27.24
AF 238	22.40	1.07	0.09	1.28	31.03	33.06	24.11
AF 242	16.54	1.10	0.08	1.15	23.93	17.41	16.25
Aero 5415	20.58	1.01	0.08	1.25	27.34	27.44	21.99
Aero 5500	21.97	1.10	0.08	1.33	31.80	29.29	24.97
Flotation Conditions							
Conditioning Time:		5 minutes					
Frother MIBC:		30 g/ton					
Collector Amount:		30 g/ton					
CaO:		2500 g/ton					
pH:		11.0					
$ZnSO_4$:		250 g/ton					

Although different type of collectors casused, a slight difference in metal grades and recoveries of concentrate, none of them was not succesfull to produce concentrate with acceptable grade and recovery.

The bulk flotation of copper and lead was unsuccessful with respect to both grade and recovery of concentrate. This was most probably due mineralogical character of tailing sample. Both galena and oxidized galena particles are locked in sphalerite and pyrite as well as some gangue minerals. During the depression of pyrite and sphalerite minerals, galena particles were also depressed.

4.1.1.3. Effect of Collector Dosage

A series of flotation tests with varying 3418-A (aerophine type collector) dosage were carried out. Test results were tabulated in Table 5.

Table 5. Effect of Collector Dosage in Cu-Pb Bulk Flotation

Collector Dosage (g/ton)	Cu-Pb Froth Product						
		Grade			Recovery		
	Weight (%)	Pb %	Cu %	Zn %	Pb%	Cu%	Zn%
15	18.28	1.27	0.08	1.36	30.55	24.37	21.24
30	25.50	1.02	0.07	1.25	34.22	29.75	27.24
60	27.01	0.97	0.07	1.23	34.47	31.51	28.39

Flotation Conditions
Conditioning Time: 5 minutes
Frother MIBC: 30 g/ton
CaO: 2500 g/ton
pH: 11.0

As seen from Table 5 additon of more than 30 g/ton 3418A as a collector was not resulted a significant increase on metal grade and recoveries of Cu-Pb bulk concentrates.

4.1.1.4. Effect of $ZnSO_4$

In order to examine the effect of $ZnSO_4$ dosage as depressant for sphalerite mineral, $ZnSO_4$ dosage was increased to 500 g/tons. The test results are tabulated in Table 6.

Table 6. Effect of $ZnSO_4$ Addition in Cu-Pb Bulk Flotation

$ZnSO_4$ (g/ton)	Cu-Pb Froth Product						
	Weight (%)	Grade			Recovery		
		Pb %	Cu %	Zn %	Pb%	Cu%	Zn%
250	25.50	1.02	0.07	1.25	34.22	29.75	27.24
500	12.16	1.07	0.07	1.17	17.60	14.19	12.16

Flotation Conditions
Conditioning Time: 5 minutes
Frother MIBC: 30 g/ton
Collector 3418 A: 30 g/ton
CaO: 2500 g/ton
pH: 11.0
ZnSO4: 250 g/ton

An increase in the dosage of $ZnSO_4$ addition resulted a slight decrease on zinc content of lead-copper concentrate while the decrease in the amount of bulk concantrate was significant. This adverse effect of $ZnSO_4$ addition was again due the minerological texture of tailing. During the depression of sphalerite interlocked sphalerite, copper, sphalerite-pyrite and sphalerite, galena were also depressed.

4.1.1.5. Effect of Sulphidizing Agent

The degree of oxidation in lead and copper minerals is important for the success of flotation. For oxidized and tarnished minerals, addition of sodium sulfide and sodium hydrosulfide as sulfidizing agent may be helpfull. During tests, the dosage of sulfidizing agent NaHS were varied between 25 g/ton to 500 g/ton.

The results of the experiments are given in Table 7. And Figure 13. As can be seen from these results 250 g/ton NaHS addition as sulfidizing agent gave the highest recovery in the tests. However, the lead and copper grade of bulk concentrate was not in promising level.

Table 7. Effect of NaHS addition in Cu-Pb Bulk Flotation

NaHS (g/ton)	Cu-Pb Froth Product						
	Weight (%)	Grade			Recovery		
		Pb %	Cu %	Zn %	Pb%	Cu%	Zn%
25	26.41	1.08	0.08	1.08	37.53	35.21	24.38
50	31.63	1.09	0.08	1.10	45.36	42.17	29.73
100	36.49	1.00	0.08	1.12	48.01	48.53	34.93
250	40.18	1.08	0.08	1.07	57.10	53.57	36.74
500	36.91	1.08	0.08	1.16	52.45	49.21	36.59

Flotation Conditions	
Conditioning Time:	5 minutes
Collector Amount:	30 g/ton
CaO:	2500 g/ton
Frother MIBC:	30 g/ton
pH:	11.0

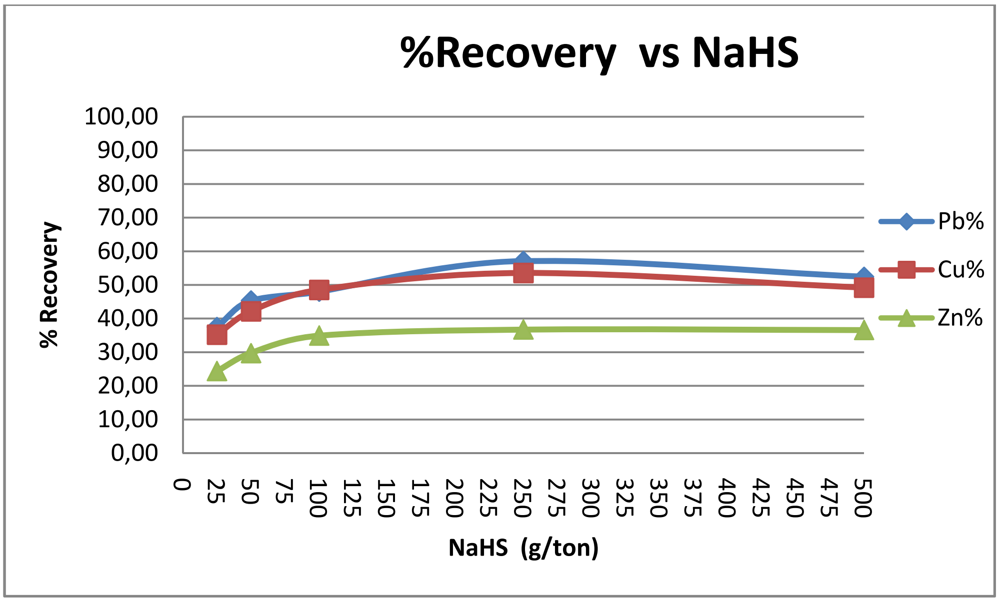


Figure 13. Effect of NaHS Dosage on the Pb, Cu and Zn Recoveries

4.1.1.6. Effect of NaCN+$ZnSO_4$ Addition in Cu-Pb Bulk Flotation

A single flotation test was conducted where NaCN+$ZnSO_4$ combination (50 g/ton + 250 g/ton) was used as depressant agent. During this test pH was adjusted to 11 with additon of 2500g/ton CaO, 30 g/ton 3418-A was used as collector, 250 g/ton NaHS was used as sulfidizing agent. No improvement was observed in depression of sphalerite and pyrite minerals.

4.1.1.7. Effect of Grinding in Cu-Pb Bulk Flotation

To produce fresh particle surfaces, the test sample was ground in ball mill for a very short period. This grinding increased the – 74 micron fraction amount of test sample from 85% to 87% . Table 8. shows the test results conducted at same flotation conditions for orginal tailing sample and slightly grund tailing sample.

Table 8. Effect of regrinding in Cu-Pb Bulk Flotation

Feed	Cu-Pb Froth Product						
	Weight (%)	Grade			Recovery		
		Pb %	Cu %	Zn %	Pb%	Cu%	Zn%
Ground Sample	25.67	1.11	0.11	1.86	37.49	47.06	40.81
Original Sample	28.34	1.49	0.09	1.60	55.56	42.51	38.75

Flotation Conditions	
Conditiotining time:	10 min
Collector:	Mixture of KAX + 3418A + AF242 (25g/ton)
Depressants:	50 g/ton NaCN + 250 g/ton ZnSO4
Dispersant:	Na2SiO3 (50 g/ton)
pH:	11
CaO:	2500g/ton
Sulfidizing Agent:	NaHS (50 g/ton)
Frother:	MIBC

The results shown in Table 8 indicated that the removal of the oxide layer from the particle surface did not improve the grade and recovery of concentrate. Both recoveries and grades of the concentrate were all below the market specification for the targeted metals. Therefore, the studies for production of copper-lead bulk concentrates were abandoned.

4.1.2. Production of Lead-Copper-Zinc Bulk Concentrate

A series of flotation tests were conducted to produce Pb-Cu-Zn bulk concentrate.

4.1.2.1. Effect of $CuSO_4$ Addition

In this group of tests $CuSO_4$ is used as an activating agent for sphalerite. These tests were completed in two stages. At the first stage, sulphide forms of valuable minerals were tried to be floated then with the addition of sulphidizing agent minerals with oxidized and tarnished surfaces were floated. After combining two concentrates chemical analyses was done. Test results were tabulated in Table 9 and shown in Figure 14.

Table 9. Effect of $CuSO_4$ Addition in Pb-Cu-Zn Bulk Flotation

CuSO4 (g/ton)	Cu-Pb Froth Product						
	Weight (%)	Grade			Recovery		
		Pb %	Cu %	Zn %	Pb%	Cu%	Zn%
100	30.48	1.24	0.11	2.20	49.73	55.88	57.31
250	35.46	1.28	0.11	1.97	58.00	63.17	59.71
500	44.81	1.24	0.10	1.68	66.58	74.81	64.34

Flotation Conditions
First Stage:
Collector: KAX+ AF-242+3418 A(10+20+20 g/ton)
Dispersant: Na2SiO3 (50g/ton)
Frother: MIBC 15g/ton

Second Stage:
Activator: CuSO4 (100g/ton)
Sulfidizing Agent: NaHS (100g/ton)

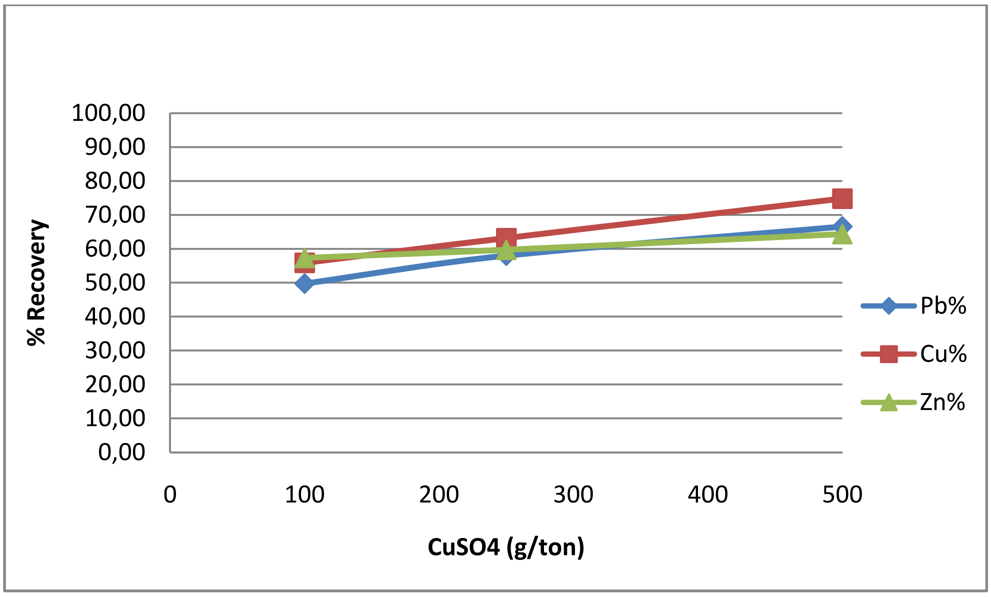


Figure 14. Effect of $CuSO_4$ Dosage on Grade and Recovery of Pb-Cu-Zn Bulk Concentrate

As seen from Table 9, Zn recovery in bulk concentrate increases with increasing amount of $CuSO_4$ addition. $CuSO_4$ has also positive effect on recovery of lead and copper metal in bulk concentrate. This was probably due to activating effect of $CuSO_4$ on oxidized lead and copper minerals. But the activating effect of $CuSO_4$ on pyrite minerals prevented the selectivity of process, and resulted concentrate with low grades.

4.1.3. General Remarks of Flotation Studies

The flotation tests were unsuccesful. Recoveries were very low, with the highest being 66.58%, 74.81% and 64.34% respectively for lead, copper and zinc. The grades were even lower. Extremely fine intrusion of valuable minerals in pyrite and gangue minerals was the main reason for the low grade and recovery of the concentrate. Intensive oxidation of mineral surfaces was the other reason for poor selectivity.

4.1.4.Leaching Studies

A series of leaching tests were conducted with different sulfuric acid concentration at different time intervals for representative tailing samples. Dissolution mechanisms of the minerals in sulfuric acid medium are as follows:

For Sphalerite mineral;

$ZnS + H_2SO_4 + \frac{1}{2} O_2 \rightarrow ZnSO_4 + H2O + S^\circ$

For Pyrite mineral;

$2FeS_2 + 3/2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2SO_4 + S^\circ$

$FeS_2 + 7 FeS_2(SO_4)_3 + 8H_2O \rightarrow 15 FeSO_4 + 8 H_2O$

For PbS Mineral;

$PbS + H_2SO_4 \longrightarrow PbSO_4 + H_2S$

$PbS + Fe_2(SO_4)_3 \longrightarrow PbSO_4 + FeSO_4 + S°$

For $CuFeS_2$ mineral;

$CuFeS_2 + H_2SO_4 + O_2 \longrightarrow CuSO_4 + FeSO_4 + S° + 2H_2SO_4$

$2FeSO_4 + H_2SO_4 + ½\ O_2 \longrightarrow Fe_2(SO_4)_3 + H2O$

$CuFeS_2 + 2Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 5FeSO_4 + 2\ S°$

4.1.4.1. Effect of Leaching Time

The effect of leaching time was investigated by varying times between 15 to 180 minutes. Leaching recoveries (or Extraction%) of Zn metals are given in Table 10 and presented in Figure 15. The results indicated that after leaching time of 120 minutes, no further significant improvement in the recovery was observed.

During these tests, acid concentration, solid%, leaching temperature was kept constant.

Table 10. Effect of Leaching Time on the Zn Recovery.

Leaching Time (Minute)	Zn Recovery (%)
15	19.58
30	37.3
45	41.77
60	50.09
90	73.38
120	78.71
180	79.12
Leaching Conditions: H_2SO_4 Concentration: 75 g/lt H_2SO_4 Volume: 200 cc Sample Amount: 25 g Temperature: Room Temperature	

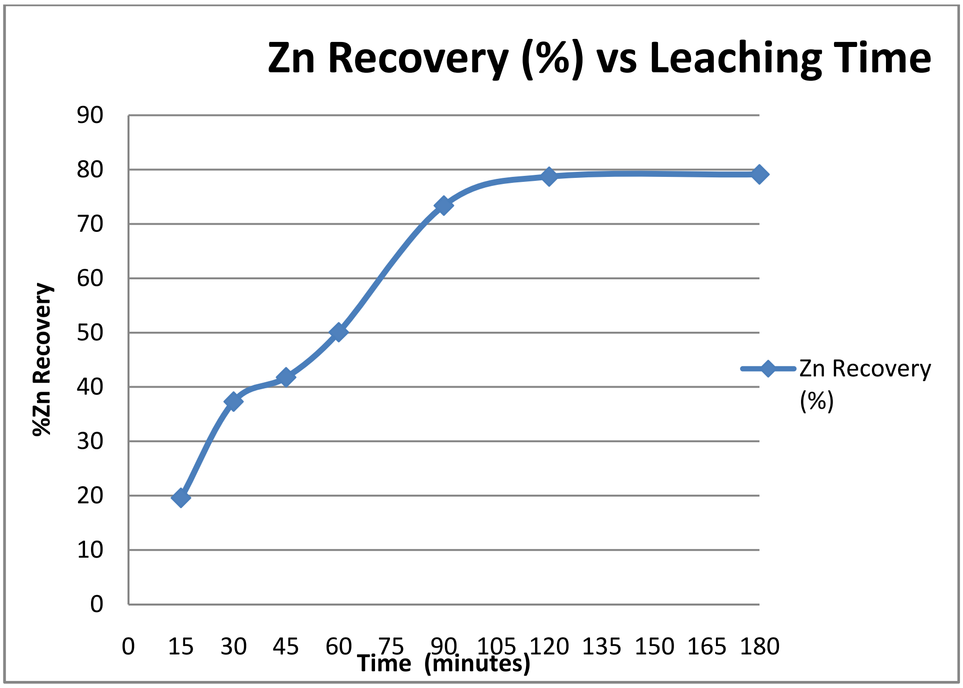


Figure 15. Effect of Leaching Time on the Zn Recovery

4.1.4.2. Effect of Acid Concentration

The effect of H_2SO_4 concentration was investigated by varying acid concentration between 75 g/lt to 175 g/lt. The acid concentration of 75 g/lt, 125 g/lt and 175 g/lt were equiavalent to 0.76 M, 1.28 M and 1.79 M, respectively. Leaching recoveries of Zn metal during these tests are tabulated in Table 11 and presented in Figure 16 and 17.

Table 11. Effect of Acid Concentration on Zn Recovery.

Leaching Time (min.)	Zn Recoveries %		
	75 g/lt (0.76M) H_2SO_4	125 g/lt (1.28 M) H_2SO_4	175 g/lt (1.79 M) H_2SO_4
15	19.58	39.21	49.18
30	37.30	47.33	56.28
45	41.77	50.58	67.54
60	50.09	63.07	71.34
90	73.38	77.33	75.96
120	78.71	77.01	79.14
180	79.12	79.24	80.62
Leaching Conditions H_2SO_4 Volume: 200 cc SampleAmount: 25 g Temperature: Room Temperature			

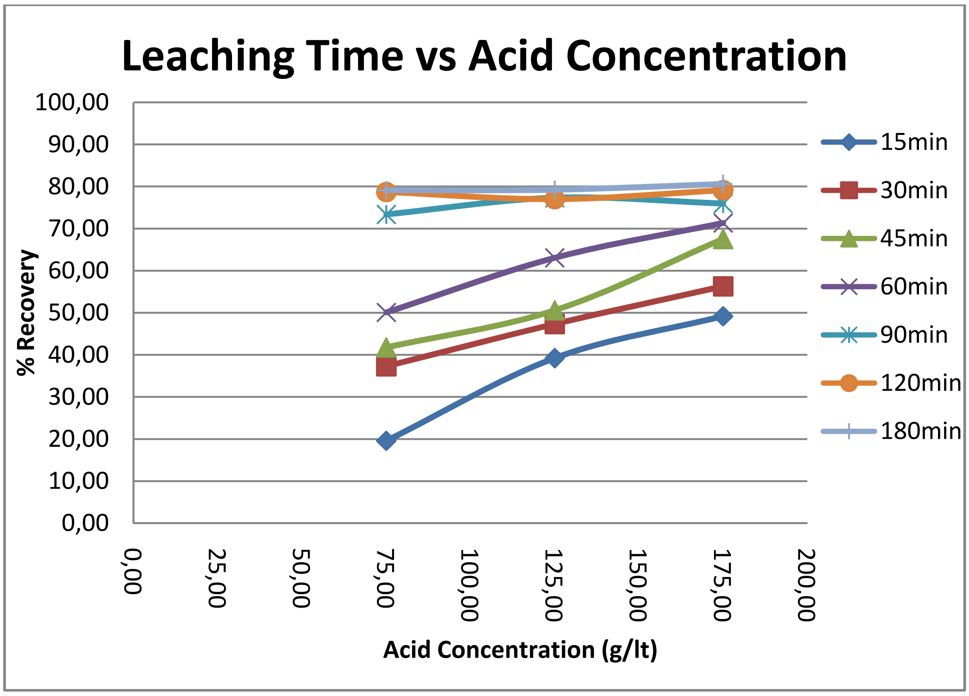


Figure 16. Extraction of Zn at Different H_2SO_4 Concentration

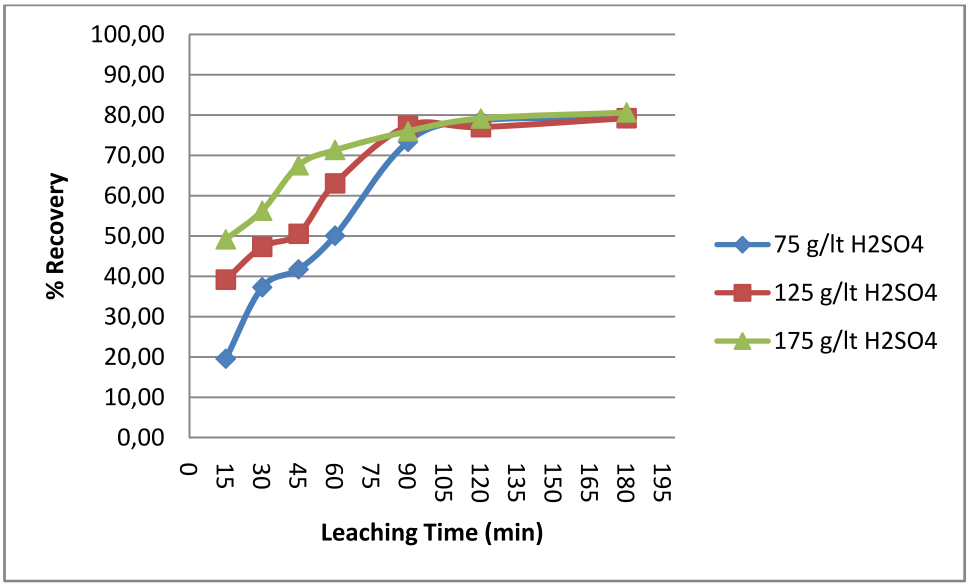


Figure 17. Extraction of Zn at Different Leaching Time

As seen from the results in Figure 16 and 17, acid concentration increases the Zn recovery and acid concentration is more effective for extraction of Zn from the tailing sample at the beginning of leaching period. As the leaching period increases, the effect of H_2SO_4 concentration on Zn extraction was decreased.

4.1.4.3. Effect of Leach Solution Volume

Pulp density is an important leaching parameter in terms of leaching kinetics. Therefore, to determine the effect of this parameter on the recovery of zinc, the sample is leached in 200 cc, 300 cc and 400 cc acid solution volume with same acid concentration during 1 hour leaching period. The percent solid pulp densities were calculated as 11.76%, 8.16% and 6.24% by weight considering 200 cc, 300cc and 400 cc acid solution volume, respectively. The solution volume (pulp density percentages) and zinc recovery percent are tabulated in Table 12. Results are presented in Figure 18 and 19.

Table 12. Effect of Leach Solution Volume and Pulp Densities on Zinc Recovery

Solution Volume (cc)	Pulp Density (%) by w/w	Zn Recovery (%)
200	11.76	63.07
300	8.16	66.29
400	6.24	64.52

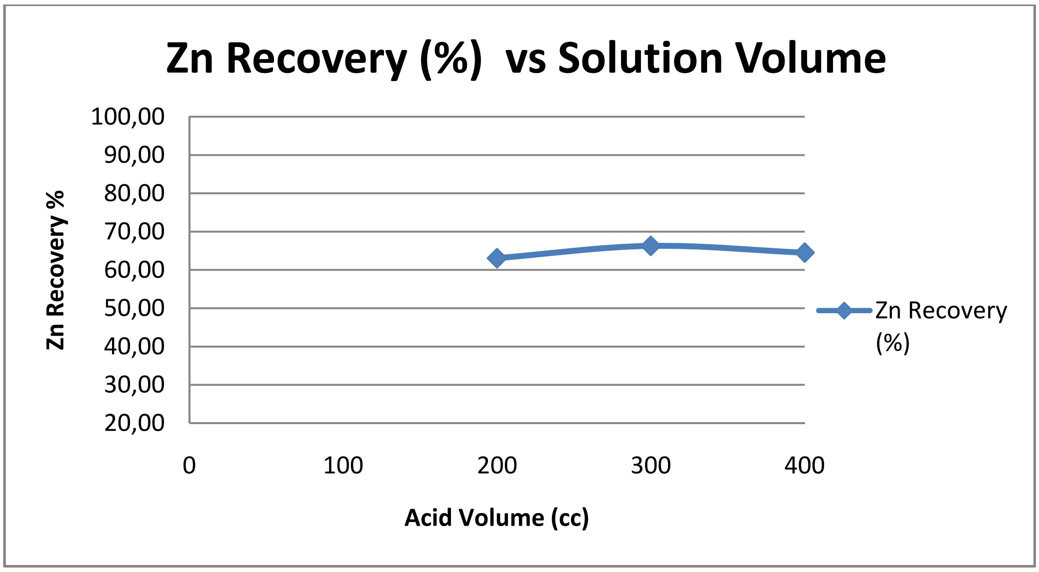


Figure 18. Effect of Acid Solution Volume (125 g/lt H_2SO_4 concentration, 1 hr leaching).

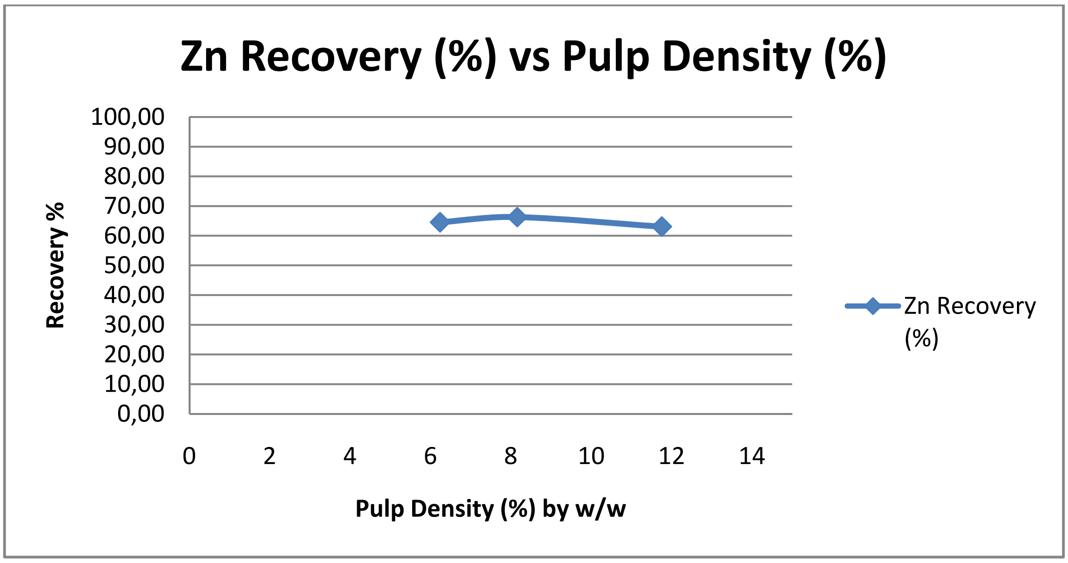


Figure 19. Effect of Pulp Density % (125 g/lt H_2SO_4 concentration, 1 hr leaching).

As seen from Figure 19, pulp density has no significant effect at the examined pulp density range.

4.1.4.4. Effect of Temperature

It is well known that the temperature is one of the most important parameter that affect leaching process. In this study the effect of temperature was examined at temperature of 40 °C, 60 °C and 80 °C. During the leaching tests, leaching solution concentration (125 g/lt H_2SO_4), leaching duration (120 minutes), leaching solution volume (200 cc) were kept constant. The results of the tests are tabulated in Table 13 and presented in Figure 20. The test results indicated that the increase in the temperature from room temperature to elevated temperatures increase the recovery of zinc revovery from 77% to 90%.

Table 13. Results of leaching tests at Elevated Temperature.

Temperature (°C)	Zn Recovery (%)
Room Temperature (20°C)	77.01
40	81.07
60	88.26
80	89.99

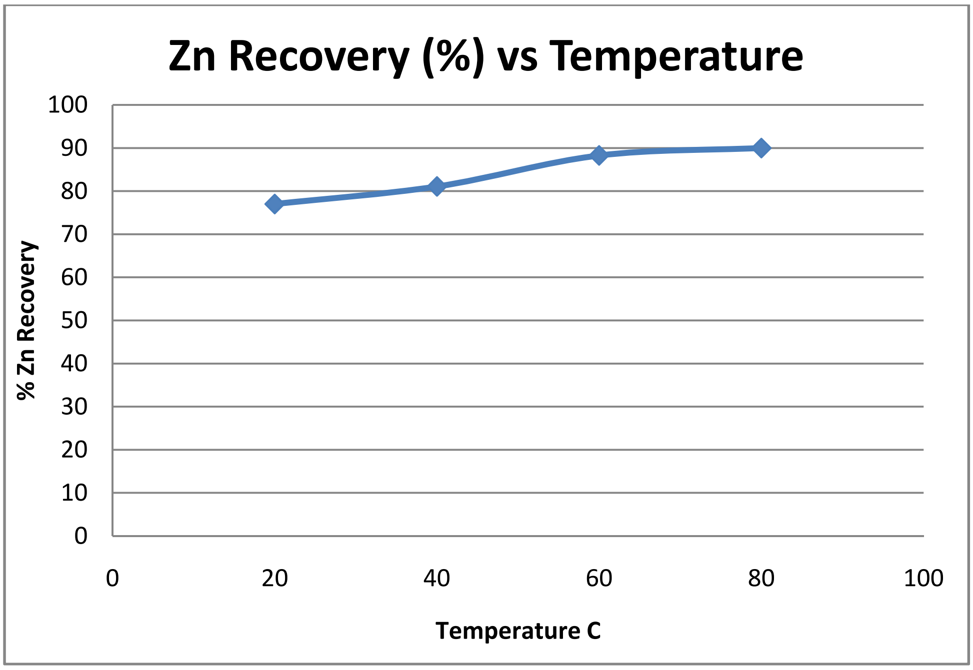


Figure 20. Effect of Temperature at Elevated Temperature

4.1.4.5 General Remarks on Leaching Test Results

Leaching tests on the test sample have shown that zinc can be selectively extracted from the sample while lead report to the residues as $PbSO_4$. The dissolution rate of zinc was depend on, leach duration, acid concentration and leaching temperature.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn in the light of the tests performed on a tailing sample from Kosovo Artana tailing dump.

1- The major ore minerals in the sample is pyrite. Chalcopyrite, sphalerite, galena and their oxidized products are also found in minor amounts in the sample.

2- All minerals are very finely interlocked with each other.

3. Flotation is not a promising concentration technique for Kosovo Artana tailings which are characterized with complex composition of intergrowth of zinc and galena with pyrite and other gangue minerals.

4. H_2SO_4 leaching at elevated temperature is the promising leaching process for extraction of zinc from tailings of Kosovo Artana Concentrates,

5. 90% Zinc extraction is possible with H_2SO_4 the leaching at leaching temperature of 80 °C.

6. The economical validity of H_2SO_4 leaching has to be investigated with pilot-scale test works.

7. Effect of roasting on Zn extraction has to be examined with H_2SO_4 leaching.

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