BENEFICIATION OF CARBONACEOUS LEAD AND ZINC ORES BY A COMBINED FLOTATION AND LEACHING METHOD

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

SENA SARILAR

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
MINING ENGINEERING

SEPTEMBER 2019

Approval of the thesis:

BENEFICIATION OF CARBONACEOUS LEAD AND ZINC ORES BY A COMBINED FLOTATION AND LEACHING METHOD

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ABSTRACT

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Master of Science, Mining Engineering
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September 2019, 152 pages

Within the scope of this thesis study carbonaceous lead and zinc ore obtained from Yozgat – Akdağmadeni region of Turkey was used. Main objective of the study is to obtain lead concentrate at possible maximum grade and recovery rates by using conventional flotation beneficiation method. In addition to that second main motivation of the study is the extraction of zinc from flotation tailing by using hydrometallurgical method named as leaching under a range of experimental conditions by using different types of leaching reagents. According to chemical analysis of run of mine material, the ore contains 3.17% Pb, 6.19% Zn and 6.72% Fe, 4.35% Al, 23.16 % Si. As was expected, iron, aluminum and silica were observed as the main impurities, thereby efforts were focused on the rejection of these elements. Moreover, mineralogical analysis indicated that the major zinc bearing minerals are smithsonite (zinc carbonate) and willemite (zinc silicate) in addition to that major lead mineral is cerussite (lead carbonate). Within the scope of present study, cerussite concentrate having 60.20% Pb grade at 64.29% recovery rate by using 250 g/t Na_2SiO_3 as dispersant (conditioned for 10 minutes), H_2SO_4 as pH regulator, 4000 g/t Na_2S as sulfidizer agent (conditioned for 15 minutes), 500 g/t PAX as collector (conditioned for 10 minutes) and 75 g/t F-533 as frother was applied. In order to obtain maximum possible grade at a maximum reasonable recovery value 3 cleaning stages without additional reagent were applied. Following, by using flotation tailing as feed material for leaching tests 60 leaching test by using sulphuric acid, ammonia, ammonium carbonate, ammonium chloride, citric acid and boric acid were conducted under range of variable operational parameters. With the consideration of performed leaching tests statistical models were constructed in order to determine optimum leaching parameters and leaching reagent which provide maximum zinc extraction ratio with rejection of impurities. From the this point of view ammonium chloride leaching provided maximum reasonable technical zinc extraction rate as 86.17% rate by using 5 M ammonium chloride at 90°C with leach duration as 60 minutes. From the industrial applicability point of view sulphuric acid leaching would be considered as best solution since 96.63% Zn was extracted rates by using 1M sulphuric acid at 30°C with leaching duration as 60 minutes.

Keywords: Cerussite, smithsonite, flotation, leaching

ÖZ

KARBONATLI KURŞUN – ÇİNKO CEVHERİNİN FLOTASYON VE LİÇ METHODLARI İLE ZENGİNLEŞTİRİLMESİ

Sarılar, Sena
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Tez Danışmanı: Prof. Dr. Mustafa Ümit Atalay

Eylül 2019, 152 sayfa

Bu tez çalışması kapsamında kullanılan cevher Yozgat – Akdağmadeni bölgesinden alınmıştır. Çalışmanın temel amacı, mümkün en yüksek tenör ve randıman ile konvansiyonel flotasyon metodu kullanılarak kurşun konsantresi elde etmektir. Bununla birlikte, çalışmanın ikinci temel amacı, yapılan flotasyon deneylerinden elde edilen artık malzemeden hidrometalurjik yöntemler kullanılarak çinkonun kazanılmasıdır. Liç deneyleri çeşitli operasyonel koşullar altında farklı kimyasallar kullanılarak gerçekleştirilmiştir. Tüvenan cevherin kimyasal analiz sonuçlarına göre, cevher %3.17 Zn, %6.19 Pb ve %6.72 Fe, %4.35 Al, %23.16 Si içermektedir. Beklenildiği gibi demir, aluminyum ve silis temel safsızlıklar olarak belirlenmiş ve çalışmada bu safsızlıkların uzaklaştırılmasına odaklanılmıştır. Ayrıca, cevherin mineralojik analiz sonuçlarına göre, ana çinko minerali smitsonit olarak belirlenmiş ve cevherin hemimorfit, vilemit gibi çinko minerallerini de az miktarda da olsa ihtiva ettiği tespit edilmiştir. Bununla birlikte temel kurşun mineralinin serüzit olduğu anlaşılmıştır. Bu çalışma kapsamında, konvansiyonel flotasyon methodu kullanılarak %60.20 tenörlü kurşun konsantresi %64.29 verimle elde edilmiştir. Flotasyon çalışmaları esnasında 250 g/t Na_2SiO_3 dağıtıcı olarak (10 dakika kondisyonlama süresi ile), H_2SO_4 pH düzenleyici olarak, 4000 g/t Na_2S canlandırıcı olarak (15 dakika kondisyonlama süresi ile), 500 g/t PAX toplayıcı olarak (10 dakika kondisyonlama süresi ile) ve 75 g/t F-533 köpürtücü olarak kullanılmıştır. Mümkün en yüksek konsantre tenörü elde edilmesi amacıyla, verim değerinin de makul bir seviyede tutulması hedeflenerek kaba flotasyondan sonra herhangi bir kimyasal eklemeden üç aşamalı temizleme flotasyonu gerçekleştirilmiştir. Sonrasında, flotasyon artığı besleme malzemesi olarak kullanılarak çinko kazanımı amacıyla farklı liç kimyasalları ile belirli değişken operasyonel koşullar altında 60 adet liç deneyi gerçekleştirilmiştir. Liç deneyleri kapsamında kullanılan kimyasallar, sülfürik asit, amonyak, amonyum klörür, amonyum karbonat, sitrik asit ve borik asittir. Maksimum çinko kazanımını en az safsızlık çözünürlüğü ile sağlayan optimum deney koşullarının ve liç kimyasalının belirlenmesi amacıyla deney sonuçları kullanılarak istatistiksel model oluşturulmuştur. Tüm bunlar göz önünde bulundurulduğunda %86.17 çinko kazanımını sağlayan amonyum klörür liçi teknik olarak uygulanabilir olarak belirlenmiştir. İstatistiksel program tarafından bahsedilen sonuçları veren optimum deney 5M amonyum klörür kullanılarak 90°C sıcaklıkta 60 dakika deney süresi olan liç çalışması olarak belirlenmiştir. Çalışmaların endüstriyel uygulanabilirliği göz önüne alındığında, sülfürik asit kullanılarak gerçekleştirilen ve %96.26 çinko kazanım sağlayan deney, bu cevher için en iyi yöntem olarak belirlenmiştir. İstatistiksel program tarafından bahsedilen sonuçları veren optimum deney 1M sülfürik asit kullanılarak 30°C sıcaklıkta 60 dakika deney süresi olan liç çalışması olarak belirlenmiştir.

Anahtar Kelimeler: Serüzit, smitsonit, flotasyon, liç

TO THE MEMORY OF ŞİRİN SARILAR

ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude and appreciation to my supervisor, Prof. Dr. Mustafa Ümit Atalay for his supervision, support, patience, and continuous guidance in preparation of this of this thesis. In addition, I am also grateful to Prof Dr. Naci Emre Altun for his help during my studies. The examining committee member, Associated Prof. İlkay B. Can is also greatfully acknowledged for her valuable contributions and for serving on the M.Sc. thesis committee.

I must express my special thanks to Yiğit Altınsel for his support, help, contribution and motivation during thesis study and experimental tests. I would like to thank my friends and colleagues; Dr. Mustafa Erkayaoğlu, Dr. Selin Yoncacı, Ceren Karataş Batan and Enver Yılmaz, Mahir Can Çetin and Selami Uğur Üst for their support and motivation.

I would also like to thank to META Nikel-Kobalt A.Ş. (Dr. Orhan Yılmaz, Yücel Yalçınoğlu, Nuray Demirel, Ruhi Çiçek, Dr. Şerif Kaya, Erdem Dikyar and Fahri Can Maral).

Finally, I owe my greatest thanks to my father Erhan Sarılar and my brother Emin Sarılar for their endless support and encouragement during my hard times.

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INTRODUCTION

1.1. General

Mining supplies all the basic resources used by modern civilization. Mineral processing follows mining and provides opportunity to extract valuable minerals from run of mine to obtain commercial end products.

Minerals can be classified as metallic and non-metallic according to the usage areas and physical properties of them. Briefly metallic minerals could be classified as composed of metals with high specific gravity and metallic luster. Lead and zinc are very widespread used metals in daily life from past to present and have crucial commercial importance in industry. In general point of view, lead either by itself or its chemical alloys utilized almost through the humankind history. The chemical symbol for lead ‘Pb’ comes from the Latin term ‘plumbum’ which means ‘water work’ referring back to ancient times when lead was used for construction of water pipes. Athens notices lead deposit 2600 years ago and foundation of these lead deposit was keystone for their economy (Christie & Brathwaite, 1995). Exact evidence which proves utilization of lead belongs to Egyptians, Greeks and Romans in ornaments, weights, solder and water pipes.

As time progressed lead mining was improved and important lead deposits were developed during middle ages in Spain, Sweden and Eastern Europe (Christie & Brathwaite, 1995). In these days and ages lead also have important role and diversified amount of usage area like storage battery, anti-knocking additive, cable sheathing, vibrating damping, radiation shielding, bullets and shots, acid tanks, plumbing, roof sheeting, solder, pigments, oil drier, hand-set printing, glass and miscellaneous alloys (Chatterjee, 2007). As in the case of lead, zinc also has known and used for a long while. The name zinc was derived from the Greek term ‘zink’. Zinc was benefited among Roman times especially in combination with copper as the alloy brass. The Indian metallurgist isolated zinc metal as early as 13th century, and Chinese has achieved large scaled production of zinc by the 16th century (Christie & Brathwaite, 1995). Fundamental zinc deposits developed along the Medieval Period in Spain, Cornwall, Sweden, Saxony and some areas of Eastern Europe. Although zinc was known and used by its chemical alloys in the past, it has wide utilization area either as metal and alloy in nowadays as die casting, galvanization, rolled products, alloys, oil drier, dry cell, alkaline battery, gold recovery, human diet and pyrotechnics (Chatterjee, 2007). Considering all these, as it was aforementioned lead and zinc are among the oldest and essential metals used and their importance scale up day by day in today’s word. By taking into account all of these, lead-zinc production rates, methods and processing technologies tried to be improved in the world to provide required amount of these metals in adequate quality. Production rates and reserve amounts of lead and zinc for presider countries are presented in Table 1.1 and Table 1.2 (Mineral Commodity Summaries, 2019)

Table 1.1 Lead production rates and reserve amounts of presider countries in the World (Mineral Commodity Summaries, 2019)

	Mine Production ($\times 10^3$ tons)		**Reserve ($\times 10^3$ tons)**
	2017	**2018**	
United States	310	260	5,000
Australia	459	450	24,000
Bolivia	110	100	1,600
China	2,150	2,100	18,000
India	170	170	2,500
Kazakhstan	112	100	2,000
Mexico	243	240	5,600
Peru	307	300	6,000
Russia	200	200	6,400
Sweden	74	70	1,100
Turkey	68	60	6,100
Other Countries	379	380	5,000
World Total	4,580	4,400	83,000

Table 1.2 Zinc production rates and reserve amounts of presider countries in the World (Mineral Commodity Summaries, 2019)

	Mine Production ($\times 10^3$ tons)		**Reserve ($\times 10^3$ tons)**
	2017	**2018**	
United States	774	790	11,000
Australia	842	940	64,000
Bolivia	473	520	4,800
Canada	344	340	3,000
China	4,400	4,300	44,000
India	833	800	10,000
Kazakhstan	330	390	13,000
Mexico	674	650	20,000
Peru	1,470	1,600	21,000
Sweden	251	220	1,400
Other Countries	2,140	2,300	33,000
World Total	12,500	13,000	230,000

There are variety of lead and zinc minerals occur in nature. The most common economic mineral of lead found as lead sulphide (PbS), namely galena, which sometimes turn into Cerusite ($PbCO_3$) and Anglesite ($PbSO_4$) (Chatterjee, 2007). In addition to these, there are 55 known zinc minerals, but only few of them are economically viable. The chief zinc mineral is Sphalerite (ZnS) providing %85 of zinc production. Other main secondary zinc minerals are Smithsonite ($ZnCO_3$) and Willemite (Zn_2SiO_3) and Hemimorphite $(ZnOH)_2SiO_3$ (Abkhoshk, et al., 2013).

Although beneficiation and concentration methods for sulfide types of lead and zinc minerals are more economically feasible and easy to operate, due to the shortage of sulfide mineral types of these metals coupled with increased demand from developed and emerging countries cause commercial interest in non-sulfide counterparts of lead and zinc deposits (Abkhoshk et al., 2013) .For this reason at the present time, importance of oxide type deposits of lead and zinc metals are in increasing trend. As it was mentioned before, there are variety of oxide lead and zinc mineral, Table 1.3 shows list of the oxide lead and zinc minerals of economic value.

Table 1.3 Lead and Zinc Oxide Minerals of Economic Value (modified from Handbook of Flotation Reagent Volume 2)

Mineral	**Chemical Formula**	**Content (%)**	**Specific Gravity (g/cm^3)**
Cerusite	$PbCO_3$	77.0	6.5
Anglesite	$PbSO_4$	68.3	6.3
Pyromorphite	$Pb_5(PO_4)_3Cl$	75.8	6.5
Crocoite	$PbCrO_4$	64.6	5.9
Wulfenite	$Pb(MnO_4)$	55.8	7.1
Minettizite	$Pb_3(AsO_4)_3Cl$	69.5	7-7.2
Plumbojarosite and Mimetite	$PbFe_6(SO_4)_4(OH)_{12}$	18.3	4.5
Calamine (Hemimorphite)	$Zn_4(OH)_2.Si_2O_7.OH$	67.3	3.4-3.5
Clinohedrite	$Ca_2Zn_2(OH_2)Si_2O.7H_2O$	60.0	3.4-3.7
Smithsonite	$ZnCO_3$	35.0	4.3-4.4
Willemite	Zn_2SiO_4	74.0	3.9-4.2
Zincite	ZnO	20.0	5.5

In terms of mineral processing point of view, the most common and economically feasible concentration methods for sulfide types lead and zinc minerals is conventional flotation concentration method which is advantageous in terms of low reagent consumption and easy operating conditions. However, beneficiation of oxide lead and zinc mineral by using conventional flotation concentration method is more challenging than their sulfide counterparts because of operational cost due to excessive reagent consumption, and flotation which is usually results with low metallurgical grade and recovery values. The reason causes these operational and economical difficulties is, higher solubility of oxide minerals and extensive hydration of oxide surfaces which also resulted with low floatability (Fuerstenau et al., 1986). Beneficiation of oxide types of lead minerals namely Cerussite and Anglesite can be achieved by using conventional flotation methods with the help of sulfidizing agents prior to the flotation concentration (Fuerstenau et al., 1986) which provides minerals surfaces similar to metal sulfide and thus it can be recovered effectively with conventional flotation reagent such as xanthate type collectors and enhance the hydrophobicity of the mineral surface (Feng et al., 2016).

In spite of all these supportive techniques, even if flotation of oxide type lead minerals can be successful in laboratory scale, it is still challenging to obtain high metallurgical recovery and grade values with the consideration of economic feasibility limits of concentration methods in industrial scales. Furthermore, beneficiation of oxide zinc minerals by using conventional flotation method is also difficult because of the low hydrophobicity of the mineral surfaces due to excessive oxidation of surfaces. Due to that economically beneficiation of zinc oxide minerals by using conventional flotation method is hard, pyrometallurgical and hydrometallurgical methods would be alternative solution for extraction of oxide zinc minerals in economical framework. Pyrometallurgical processes involving smelting of the ore at high temperature, but there are various disadvantages resulted from this method including high energy consumption, large capital investment and production of harmful gasses (Abkhoshk et al., 2013). The other alternative method for the beneficiation of oxide zinc minerals, hydrometallurgical processes would be considered in terms of economics and satisfying recovery-grade results. Within this context, there are various parameters which effects economics and technical practicability of hydrometallurgical processes and its process efficiency namely type of solvent, type of ore, type of impurity content, temperature, stirring ratio and etc. Some of the common hydrometallurgical methods for the extraction of oxide zinc minerals would be acidic leaching and basic leaching. However as it was aforementioned efficiency of these processes depends on several parameters and these methods needed to be improved in terms of both economical and technical aspect.

1.2. Objectives and Scope of the Study

As previously mentioned, lead and zinc are among the oldest and essential metals from past to present. Primary source of these importance metals are their sulfide types minerals because of their easy and economic processing possibilities. However, sulfide type lead and zinc deposits gradually depleted which results with incrimination in importance of oxide type lead and zinc deposits with in the consideration of provision on increasing demand from developed and emerging countries for these metals (Feng, et al., 2016). On the other hand, beneficiation and concentration methods of oxide type lead and zinc minerals are not as success as methods for the beneficiation of their sulfide counterparts by using conventional techniques based on the higher solubility of oxide minerals and also to the extensive hydration of oxide surfaces (Fuerstenau et al., 1986).

The main motivation of this thesis study is, investigation and improvement of optimum processing methods in terms of both economics and technical aspects for carbonaceous lead and zinc bearing ore which is delivered from Yozgat, Turkey. The main lead mineral of the run of mine is cerussite ($PbCO_3$) while the main zinc mineral is Smithsonite ($ZnCO_3$) with the grade of 3.17% Pb and 6.19% Zn respectively. Within the scope of the present thesis studies, enrichment possibilities of lead and zinc minerals from run of mine will be evaluated under different test conditions to define optimum parameters by using different concentration techniques. During the first stage of the studies, conventional flotation concentration method will be performed in order to obtain a lead concentrate with acceptable metallurgical grade and recovery values which is also economically feasible and technically applicable. Then, with the aim of extraction of zinc from the ore by using hydrometallurgical processes, leaching tests will be performed. In the context of each experimental group different chemicals will be used as leaching reagent, i.e. sulphuric acid, ammonia and its derivatives and organic acids which can be accepted as possible feasible chemicals for similar ore types according to the previous works. Within the scope, each reagent will be applied under different operating parameters such as temperature, leaching time, solid-liquid ratio and reagent concentration to obtain economically and technically feasible conditions in order to get optimum metallurgical grade and recovery values. Consequently, the most feasible method for the enrichment of valuable minerals, besides the elimination of impurities will be determined and discussed in technical point of view.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1. Lead

2.1.1. Discovery and History

Lead is one of the most important primordial metal, which was discovered by the humankind and known from antiquity along with seven crucial metal from gold to lead. Although the lead was the base of metals, it was the most crucial factor which played role in the alchemical experiments to find philosopher’s stone which would evolve the base metals into gold. It was believed that the alchemist named the metals according to the planets – the sun was gold, the moon was silver, Jupiter was tin, Mars was iron, Venus was copper, Mercury was quicksilver and Saturn was lead (Rowe, 1983). In addition to that, as it was mentioned before the chemical symbol ‘Pb’ derived from the Latin term ‘plumbum’ due to the lead was used for the construction of water pipes in early history (Chatterjee, 2007). Probably, lead was the first metal that was extracted from an ore nearly around 9000 BC following the smelting of it at low temperatures as 300°C and used in various areas of daily life. Apart from these, one of the earliest references to lead is hanging gardens of Babylon, which is one of the seven wonders of the ancient world, are said to have been floored with sheets of lead to retain moisture for the plants growing there (Rowe, 1983). As it was indicated before, the first large lead deposit was discovered 2600 years ago in Athens and it became the one of the most important economic figure for their daily life (Christie & Brathwaite, 1995).

As the case in today’s world lead had a myriad of utilization areas in ancient times. One of the most recognized usage area of the lead in early history is in water supply system by taking the advantage of its malleability, durability and resistance to corrosion. Previously found evidences shows that lead was already used in ancient times and lead pipes used in ancient times belongs to Mesopotamia, Cyprus, Persia, Egypt, Greece, Rome and some cities of the Roman Empire. The Romans demanded large quantities of water and thus learned use of lead in water plumbing system from Greeks and used lead in water distribution system which consist of tanks, baths or vats. Other examples that prove the usage of lead in early times are related with architectural purposes as joining masonry, cesspool covering, roofing, damp-proofing of foundations, parapet walls and for opening of buildings (Cases Joses S., 2006). Utilization areas of lead and its chemical alloys, in ancient times would be enlarged with variety of examples such as ornaments, weights, solder and etc. (Chatterjee, 2007).

Although giving precise information about the historical background of lead resources and production rates during early ages was challenging, it was known that Athens used lead resources of Spain, Cyprus and Greece (Christie & Brathwaite, 1995). Significant mining activities on lead resources were performed under the control of Roman Empire and mineral resources of Portugal and Spain was evaluated by the Phoenicians and Carthaginians. In addition to these, remarkable amount of lead was produces from other European areas. Even if lead was rarely mentioned in early writings, it could be inferred that written sources indicates some amount of silver production which proves lead was produced in great amounts principally as a secondary product (Pulsifer, 1888). Based on the numismatic literature and archeological evidences, evolution of lead production during early ages in different geographical areas is given in Figure 2.1.

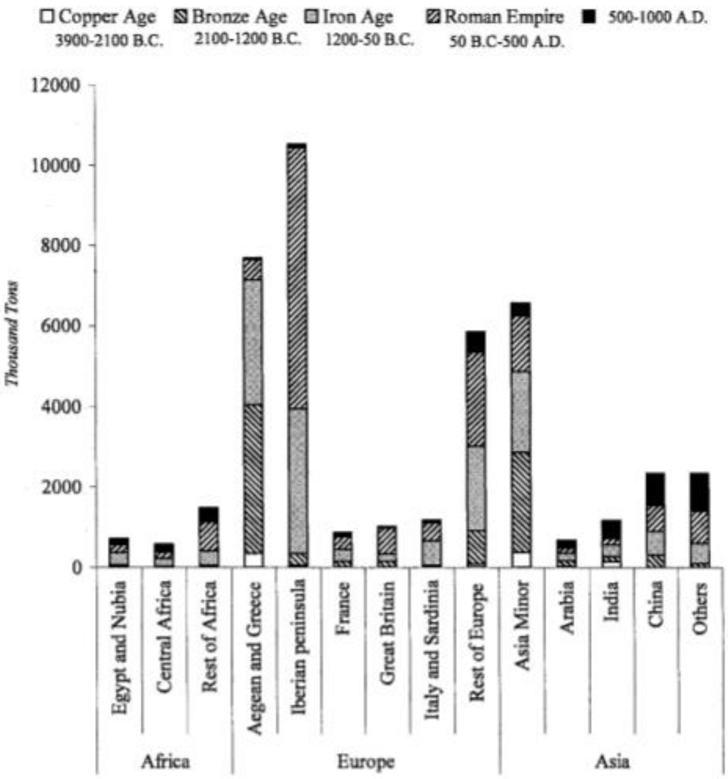


Figure 2.1 Lead Production in Ancient Word (Cases Joses S., 2006)

Only the world production of primary lead metal at the recent past has been investigated. Based on these investigations, production rate of the lead during the early part of 19th century was less than 250000 tons. Moreover, in 1880, it was enlarged to 415000 tons and increased to over one million in 1990. In 1925 lead production rates enlarged to million tons, namely to about 3.5 million tons in 1986. Finally, in the 1990s it showed downtrend and lead production rates decreased nearly 3.2 million (Chatterjee, 2007).

The first lead production in Turkey was performed in Balya-Karaaydın Mine, Balıkesir. The maximum production rates in these ore deposits was achieved at the end of 19th century and beginning of the 20th century, when it was operated under France and Greece management. Most of these mines were closed temporarily between 1918 and 1922 (Madencilik İhtisas Komisyonu, 2001).

2.1.2. Utilization of Lead

As it was the case, lead has multitudinous utilization areas in today's world by taking the advantage of the unique combination of acid resistance, softness and heaviness of lead (Chatterjee, 2007). Prominent utilization area of the lead is storage batteries which would also be named as acid battery and accumulator by using different solubility characteristics of different metals (Christie & Brathwaite, 1995). Storage batteries divided into two or more subgroup according to the type of secondary cells in a battery. The main idea for the usage of lead for batteries is the application of two different metal, which is already exposed to electrolyte and thus they produce different amount of voltage according to their solubility values. With related to this, one metal charges positively while other metal charges negatively. At the end of this process chemical energy of metal and electrolyte was converted into the electrical energy. Primary cells are obtained in the case of consumption of metals and electrolyte irreversibly, otherwise if the chemical energy could be restored through reversion of the chemical reaction with the help of electric current, the cell is called as secondary. In addition to these, anode and cathode plates of the battery were covered with PbO during neutral state in order to help charge generation (Chatterjee, 2007).

Chemical alloys of lead are important as well as lead metal itself and used in different industrial and technical applications. One of the most common example to this utilization implementation is the usage of lead as an anti-knocking additive where the ability of lead to form chemical alloys and chemical compounds are used. The working systematic of anti-knocking additives include decomposition of tetraethyl lead to a nonstoichiometric lead oxide which have the ability to trapping the HO_2 radicals which cause spark knocks (Development).

The other main utilization purpose of the lead is cable sheathing by using advantage of physical and chemical properties lead that has high density which prevents loss of high frequency radiation. In addition to that communication system for a long distance requires flexibility against to reasonable mechanical strength to any greater extent.

Lead provides this flexibility under the favor of its softness. In addition, with regarding to low melting point, softness and superior workability of lead it is already used as continues sheath around the internal conductors. The one of the other reason for the usage on lead in cable sheathing systems is its ability to protection against moisture. Moreover, by taking the advantage of having high density, lead is used for vibration damping in the construction of multistoried building and pads between the walls and also below the structure to prevent vibration caused because of the noise (Chatterjee, 2007). Another utilization area of the lead is the radiation shielding in X-Ray machines, high altitude flying aircrafts and atomic plants, due to its effective absorption of electromagnetic radiation at short wavelengths with the help of its high density (Christie & Brathwaite, 1995). As it was indicated before, one of the important property of lead is its resistance to acid. By taking the advantage of this, lead and its chemical alloys with copper and antimony used in acid tanks (Chatterjee, 2007). As was in the ancient times, lead is still used in plumbing systems due to its advantage of corrosion resistance and even for chemical transmission lead is preferred due to its resistance to acid (Christie & Brathwaite, 1995). Based on the previous applications of lead and its chemical alloys, soldering might be the example for the alloy of tin and lead for joining two pieces of a metal by process of welding. The role of lead in soldering is to softening it while tin is used for lowering the fusion temperature. Moreover lead is used as pigment by the courtesy of its corrosion resistance. At the same time, in addition to all these utilization areas lead compounds as lead soap, lead acetate and lead hydroxide are used as oil drier because of their cheapness, availableness and effectiveness. By the fact that, lead has too many utilization areas, the last key application and industrial usage is glass industry. Leaded glass is used when the glass is intended to be worked into intricate designs, and also when it is used in the optical applications for the production of high quality lenses. Within this context, softness, malleability and high density characteristics of lead are used. By taking the advantage of lead’s softness and malleability, workability of glass was further improved. Correspondingly, because of high density lead increases the glass density, refractive index of glass also increases. In consideration of all these, leaded glass performs better when it is used for optical applications (Chatterjee, 2007). Besides all these key usage areas of lead, it could be used for variety of different application purposes like bullets and shots, synthetic rubber, adhesives, glazes and etc. (Development).

2.1.3. Physical and Chemical Properties of Lead

As was known, each element has its own properties depending on their presence in nature. Physical properties of an element are the specialty of it that would be observed without converting substance to different one. In addition, chemical properties of an element can be described as how it will react with other elements and turning one substance to another. Lead has many advantages based on its superior physical and chemical properties which make it preferable in terms of economics, availability and uncomplicated way of utilization in industrial applications of daily life. Physical and chemical properties of the lead is described and examined in the following subchapters.

Physical Properties of Lead

Lead is a naturally occurring element and is located in Group IVA of the periodic table. Lead's extensive use is predominantly resulted from its low melting point and excellent corrosion resistance in the environment (Abadin H, 2007). Moreover, lead is a dense, bluish-grey metal which is malleable and ductile (Christie & Brathwaite, 1995). It has little mechanical strength, virtually no elasticity and extremely soft (Anyadike, 2002). General physical properties of lead are given in the Table 2.1.

Table 2.1Physical Properties of Lead (Cases Joses S., 2006)

Density (g/cm^3)	11.34
Melting Point / C°	327.5
Boiling Point / C°	1750
ΔH_{fusion}/ kJ.mol^{-1}	5.121
ΔH_{vap}/ kJ.mol^{-1}	179.4
Thermal Conductivity (300K) / W m^{-1}k^{-1}	35.2
Coefficient of linear thermal expansion / K^{-1}	29.1×10^{-6}
Electrical resistivity (293K) / Ohm.m	20.648×10^{-8}

Table 2.2 Physical Properties of Lead (Cases Joses., 2006) (cont'd)

Young's Modulus / GPa	16.1
Rigidity Modulus / GPa	5.59
Poisson's ratio / GPa	0.44

Any stress that is applied to the pure lead at ambient temperature would be resulted with permanent deformation of lead, due to weakness of leads interatomic bonds and its low melting point. Even though the applied load is in small amount and if it is continuous, it would cause to changes within the metal and this could be resulted with continuing creep. Actually, this situation is not as much as important in short terms as it is in long term practical applications. Because of this, in the case of utilization of unalloyed lead under continuous stress, creep strength of lead should be considered. This property of lead is difficult to measure because the required time period could be more than 20 years. Although this would be considered as a problematic feature of lead, by careful implementation and choosing the correct material for each application this disadvantage would be turned into advantage. The mechanical properties of lead such as malleability and softness makes the pure lead workable. For any application, if greater hardness, strength or creep resistance is required, lead chemical alloys should be used as an alternative material. To sum up, lead's physical properties generally provides simplicity for its utilization areas but, in the case of insufficient value of pure lead for any specific feature, as it was mentioned before, lead chemical alloys would be alternative raw material (Anyadike, 2002). Possibility to obtain proper chemical alloys according to industrial requirements depends on chemical properties of lead which are defined in the following subsection.

Chemical Properties of Lead

With the help of lead's chemical and electrochemical properties, it is useful as the most advantageous valuable material in batteries which is the one of the most common utilization area of lead. Lead shows great resistance to corrosion in acidic media, effective electromechanical behavior in various chemical environments, chemical stability in air and water. In addition to these, due to its high atomic number and stable nuclear structure, lead become one of the most crucial milestone in our daily life. (Guruswamy, 2000). Depending on the form of lead and its chemical compounds, chemical properties of it could show variations. First of all, in the form of element scarcely cut lead swiftly loses its metallic shiny lustre in moist air because of the constitution of lead (II) oxide in the surface. Further, oxide would react with CO_2 to form lead (II) carbonate which protect metal against the possible attack. In the condition of high temperature, lead would go under chemical reaction with Sulphur and halogens. Although pure water does react with lead, the element is oxidized by the joint action of oxygen and water to give Pb (II). The dissolution reaction of the metal is occurs as follows;

$$Pb(s) \rightarrow Pb_2{}^{+}{}_{(aq)} + 2e^-$$

And the formed electrons are consumed based on the following reactions;

$$1/2O_2 + H_2O_{(l)} + 2e^- \rightarrow 2OH^-{}_{(aq)}$$

Or

$$2H_3O^+{}_{(aq)} + 2e^- \rightarrow H_{2(g)} + H_2O$$

In aerated water or acidic media, these type of salts have low water solubility and can act as protective layer. This is an important case especially if lead pipes are used for transportation of drinking water because in the case of any slow reaction Pb (II) may dissolve and cause intoxication when the water is consumed.

Lead as an element has two known and common oxidation states as Pb (II) and Pb (IV). Lead is easily oxidized in water to form of Pb (II) while Pb (IV) are powerful oxidizing agents which are reduced to Pb (II). This oxidation state is the one of the most common one in the nature and shows toxic characteristics (Christie & Brathwaite, 1995). Summary of the general chemical properties of lead are given in the Table 2.2.

Table 2.3Chemical Properties of Lead (Guruswamy, 2000)

Group	14
Period	6
Block	p
Atomic Number	82
State at 20°C	Solid
Electron Configuration	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$

2.2. Zinc

2.2.1. Discovery and History

Although the zinc, as one of the most common metal which has wide range of utilization areas in today's world, it has shorter history as a base metal in comparison with lead. Throughout antiquity, zinc wasn't known as metal but known in the form of its chemical alloys by different ancient civilizations. The one of the oldest remnants which shown utilization of zinc alloys belong to Babylonia and Assyria from 3000 BC and Palestine dating from 14000 – 1000 BC. In addition, it is known that, Romans also utilize zinc's alloy brass with copper during around 200 BC (Christie & Brathwaite, 1995). Despite the fact that there is no plenitude of information about utilization of zinc and its chemical compounds during history, it was also known that zinc-copper alloys are used as jewelry from Rhodos dating approximately 500 BC (Schönnenbeck & Neumann). Since zinc occurs in the nature in the form of chemical compounds, primarily it was used in the form of zinc carbonate namely smithsonite (Schönnenbeck & Neumann). Smithsonite was unwittingly used as smelted with copper to obtain alloy which is more yellow and effective than bronze (Chatterjee, 2007). Even though the zinc minerals used since the Bronze Age, it was not plenty of time that zinc was discovered to be an element (Schönnenbeck & Neumann). Zinc was discovered as a metal in 1520 AD and started to utilized in the 17th century. Philippus Theophrastus as a physician and natural scientist clearly defined the zinc as a new material which differentiated from other metals according to its different superior properties. While some scientist thought that the term zinc comes from the Greek term ‘zink’ which has the meaning of ‘obscure origin’, according to the some other scientist the term zinc may come from Persian term ‘sing’ which means stone (Schönnenbeck & Neumann).

Along the ancient time, the main utilization purposes of zinc were making brass as the result its alloy with copper. It was believed that, in Rome between 63 BC and 14 AD, brass was produced by heating powder calamine, charcoal and granules of copper mixture but the temperature was remained below the copper melting point. However, with the usage of zinc, the temperature could reached up to copper melting point and brass smelting could be achieved in a successful manner. Similarity between gold and brass made some scientist ambitious about the production gold from other metals. In addition to that, copper zinc alloy and some zinc salts were produced for medical applications as an astringent and antiseptic even in today’s world (Anyadike, 2002). Moreover, Marco Polo between 1254 and 1324 from Venice noticed the production of zinc oxide in Persia. At that times, Persians used a zinc vitriol solution ($ZnSO_4.7H_2O$) for the treatment of eye inflammations (Schönnenbeck & Neumann).

During Medieval Period, important zinc mines were developed in Spain, Cornwall, Sweden, Saxony and some areas of Eastern Europe. However, during these times mining activities were not technically and systematically organized. In 14th century zinc mining activities started in Zawar region of Rajasthan in India but this mining operations were not organized already. At that times, zinc ores located in European countries, India and China were began to extracted. Further more, zinc mine in India has been already operated until recently . First systematic zinc mining operation was achieved in USA in 1720 and second one was in Europe in 1740. When the time comes to 1880 the world zinc production as metal was approximately 260000 tons, then which was increased over the 5 million tons in 1968 and in 1992 production rates reached nearly 7.4 million tons (Chatterjee, 2007).

In Anatolia, zinc mining activities started by Greeks, Romes, Byzantines and Seljuks in BC 400. Even though these mines were operated from time to time, only lead and silver were produced. For this reason, slag material contains more zinc than lead in those regions. Slags remained from ancient times were placed in Bolkardağ, Akdağ Mining, Gümüşköy, Balya and Anamur. Although these deposits operated in ancient times, maximum production rates were achieved after 19th century and in the beginning of 20th century under France, Italian and Greek management. Balya Simli Lead Mine is one of the most common example of these type of mines. Greatest majority of those mines were closed between 1918 and 1933. With the establishment of Mineral Research and Exploration Institute (MTA) in 1935 lead and zinc mining activities have been gained more scientific approach (Madencilik İhtisas Komisyonu, 2001).

2.2.2. Utilization of Zinc

Based on the low awareness of the zinc as a metal and low technology in zinc mining, utilization areas of zinc as a metal was limited in ancient times, therefore it has several utilization areas in terms of different purposes in daily life and industrial applications in today's world. According to the data taken from International Lead and Zinc Study Group, main utilization purposes of zinc with respect to percentage distribution demonstrated in Figure 2.2.

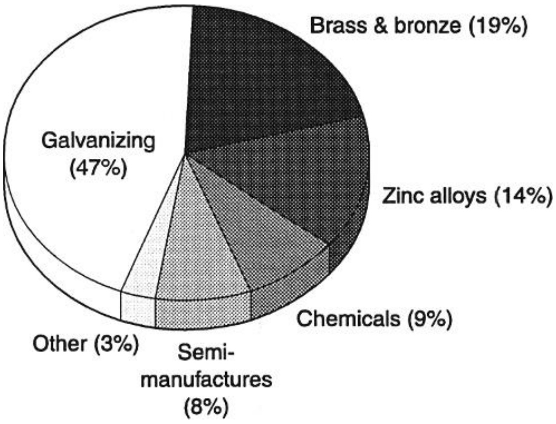


Figure 2.2 Main Utilization Areas of Zinc (Group, 2019)

One of the most prominent utilization area of the zinc is die casting which basically refers to pouring molten metal into a mould for the further usage purposes. High purity of zinc is required for die casting rather than other utilized metals such as lead, cadmium, tin, iron and titanium due to the superior parameters provided by zinc based on from its superior physical and chemical properties. Firstly, zinc provide low melting point which helps melting of a metal in terms of economy and easiness. Secondly, low viscosity of liquid zinc supply smooth unhindered flow of the molten metal into all edges of the mould under relatively low pressure and temperature. Thanks to the low temperature and pressure values, possibility to use inexpensive dies made from standard steel increases. Glabrous cooling of zinc also provides products without any pits or crack, so the subsequent matching or finishing operations are not required (Chatterjee, 2007). Even if they required, by using malleability of zinc, this process could be handled easily. The other main utilization area of zinc is galvanization which is almost equal to zinc coating based on the general meaning of galvanization that coating of iron surface by zinc with the help of some methods which are covering the surface with zinc electrolytically, defaming the material in molten zinc, repelling molten zinc on to the surface, and subjecting the surface to the zinc vapour. Reason for the usage of zinc in galvanizing process is resulted from its superipor properties. One of the most important factor to decide on zinc for galvanizing is, zinc protect iron sheets against any corrosion including atmospheric corrosion. Secondly, shiny color and luster of zinc provide pleasant outlook for coated end product (Schönnenbeck & Neumann). Moreover, in the case of exposure of atmosphere for a long time, with the help of relevancy between zinc and CO_2 to form $ZnCO_3$, further reactions were prevented. As in the die casting process, low melting and boiling points makes the whole process economically feasible. As the last reason to use zinc rather than any other possible metal on this process is based on its low specific gravity which provides relatively lower weight of galvanized product. Further utilization purpose of the zinc is related with rolled product under the favor of soft and malleable nature of zinc which helps shaping and processing of rolled sheets. In addition, as in the ancient times, zinc alloys are still used. Also, the most common and important zinc alloy is brass. Depending on the restrictions in brass composition, zinc content would be changed. The other alloy type obtained by using zinc, copper and nickel is called as German silver or nickel silver. This chemical compound is not silver but named due to its bright appearance. Thereafter, zinc is used in magnesium based structural materials which are utilized in aircraft and car wheels, extruded bars and tubes, sand casting used in aircrafts, mechanical portions worked in textile and packaging industries, die casting of pipes and portable equipment. Moreover, zinc alloys were also used in damascene works which can also be called as the art of a metal ornamentations (Anyadike, 2002). As zinc is used widely in industry and in daily life in the form of alloy, its chemical compounds might also be used for several purposes. For example, ZnO_2 is used in terms of filling material to increase titanium dioxide pigment quality. Apart from that zinc compounds might be used in the utilization of zinc sulphidosilicate in fluorescent material and inner surface of fluorescent tubes (Group, 2019). As in the case of lead, zinc was also used as oil drier. The other branch where the zinc is preferred to utilize is dry cells, which are also known as primary or non-rechargeable cells due to its electrical conductivity feature. Zinc provide less electrochemical series in comparison to other elements as carbon and copper. In dry cells, zinc takes the role of the negative electrode while carbon or copper serve as positive electrode. On the contrary, zinc included in negative pole in alkaline batteries, while negative pole obtained from manganese dioxide. Apart from these, zinc is also used in cyanidation processes which was performed for the recovery of gold by helping the precipitation of gold or any other valuable metals. As it was indicated, zinc is one of the important metal in daily life. In addition, it has a significant role in human body. With the help of using trace amount, zinc promotes formation of insulin with the help of zinc coated proteins. Moreover it supports constitution of protein, in wound healing and blood generation (Chatterjee, 2007).

2.2.3. Physical and Chemical Properties of Zinc

Each metal is unique and differentiate from each other according to their physical and chemical properties. As it is indicated under physical and chemical properties heading of lead section, physical and chemical properties of an element determine how it presence in nature and shows the reactions with other elements. Zinc has variety of favorable physical and chemical properties which make it preferable in terms of economy, availability and convenience of the processes. In the case of evaluation of properties separately aluminum, lead and tin may be thought as more attractive than zinc but by the consideration of whole properties of zinc in a combined form, there is not any other metal that has such superior properties equal to zinc. These combined properties are crucial for many industrial application of zinc. Physical and chemical properties of the zinc is described and examined in the following subsections.

Physical Properties of Zinc

Zinc is a transition element which belongs to Group IIb of the periodic table. It is a silvery blue-grey metal having lower melting point comparing with other metals which is equal to 419.5°C and boiling point of 907°C. Depending on purity level of zinc, its brightness may vary but except for high level of purity conditions it is brittle (Porter, Zinc Handbook, 1991). Although, melting point of zinc is nearly 420°C it become malleable nearly between 120°C and 150°C which makes the zinc preferable to use in production of rolled products. Zinc is soft and malleable metal and has higher tensile strength compared to lead. Malleability of zinc increases with the increase of heat (Chatterjee, 2007). In addition, it is not effected from dry air but oxidises under the condition of moist air. Due to its resistance to atmospheric conditions, its utilization areas enlarged significantly to protect steel (Porter, Zınc Handbook, 1991). Zinc shows good conducting feature for both electricity and heat (Christie & Brathwaite, 1995). Especially, it is really advance conductor of electricity that have the capability less than % 25 of copper’s, namely the best along the all metals. There are several parameters which effects thermal conductivity of zinc as temperature and crystallographic direction. Its thermal conductivity diminishes when temperature increases and single crystals of zinc shows more attractive thermal conductivity property while polycrystalline zinc provide less thermal conductivity (Porter, Zınc Handbook, 1991). As it was mentioned in utilization section, one of the main utilization are of the zinc is galvanizing, which requires high degree of fluidity, that is provided by zinc especially in the molten form (Chatterjee, 2007). Moreover, under normal conditions, zinc is not combustible by providing advantage on its industrial applications.

According to the data taken from International Lead and Zinc Study Group general physical properties of zinc is given in the Table 2.3.

Table 2.4General Physical Properties of Zinc (Group, 2019)

Atomic Number	30
Chemical Series	Transition Metal
Density	7140 kg/m^3
Appearance	Bluish pale gray
Melting Point	420°C
Boiling Point	907°C
Heat of Vaporisation	115.3 kJ/mol
Heat of Fusion	7.3 kJ/mol
Specific Heat Capacity	390 J/(kg.K)
Electrical Conductivity	16.6 106 (m.ohm)
Thermal Conductivity	116 W (m.K)

As much as zinc is useful in several applications, its chemical compounds and alloys are important for several applications. In this context, although the zinc has higher hardness and strength values than tin or lead, these strength and hardness values are noticeably less than copper's and aluminum's. For that reason, pure zinc metal cannot been used for stress resistance purposes because of the low creep resistance. In the case of these types of situations, zinc is used after alloying with small amount of other metals (Porter, 1991). Possibility to obtain proper chemical alloys according to the industrial requirements depends on chemical properties of zinc which are defined in the following section.

Chemical Properties of Zinc

As was aforementioned, zinc included to group 12 (IIB) of the periodic table and promote +2 in all its chemical compounds. Because of placing on higher levels of electromotive series, zinc compounds are relatively stable. In general, bond of zinc compounds are covalent and also in the case of compounding with strongly electro positive metals as chlorine, bonds became more ionic. In addition to these, zinc also tends to obtain stable covalent compounds with ammonia $[Zn(NH_3)_2]^{2+}$, cyanide $[Zn(CN)_4]^{2-}$ and hydroxyl $[Zn(OH)_4]^{2-}$. In most of these cases coordination number of zinc is 4, but also it would be 6 and 5, rarely. Although salts could be formed as a result of reaction of zinc and acid due to its amphoteric nature it could also forms zincates as $[Zn(OH)_3.H_2O]^-$ and $[Zn(OH)_4]^{2-}$. Based on solubility of zinc salts are low, ability to form stable hydroxyl compositions (as $3Zn(OH)_2.ZnSO_4$ and $4Zn(OH)_2.ZnCl_2$) is important. These hydroxyl compositions would precipitate until neutralization of acid solutions of the salts (Goodwin, 2017).

Zinc has relatively higher tendency to couple with oxygen and other non-metals and it has high potential to react with dilute acids to release hydrogen (Group, 2019). Reactions between zinc and oxygen occur as follow;

$$2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO$$

In addition to that, reaction between zinc and acids is given in the below;

$$Zn_{(s)} + H_2SO_{4\,(aq)} \rightarrow Zn_{2\,(aq)} + SO_4^{2-}{}_{(aq)} + H_{2\,(g)}$$

As the result of the first reaction, zinc oxide was formed, namely ZnO which is one of the most significant zinc compound. By the reaction between zinc vapor and air, high purity zinc oxide with different crystal shapes and sizes could be obtained. In addition, with the help of its advance thermal conductivity and capacity, zinc oxide typically used for rubber industry as heat dissipater. The other zinc compound is zinc sulfate, namely $ZnSO_4$ as an intermediate compound for the production of zinc from deposits.

Another compound of zinc is zinc chloride, $ZnCl_2$ which can be obtained by direct reaction or evaporation of the aqueous solution resulted from various reactions. The main utilization area of the zinc chloride is, usage in drying agents due to its high water-absorbing feature. Although the zinc sulfide already occur in nature as the mineral, namely sphalerite, it would be obtained by treating zinc salt solution with hydrogen sulfide. Zinc sulfide has important properties and might be used industrially, even if the amount of other metals as copper, manganese, silver or arsenic is limited. These chemical compounds are utilized in X-Ray screens, clocks and watches (Britannica, 2019). Some of the most prominent zinc compounds are given in the Table 2.4.

Table 2.5 Zinc Compounds (Goodwin, 2017)

Zinc Compound	**Formula**
Acetate	$Zn(C_2H_3O_2).2H_2O$
Ammonium Chloride	$ZnCl_2.2NH_4Cl$
Diborite	$ZnO.B_2O_3.2H_2O$
Carbonate	$ZnCO_3$
Cyanide	$Zn(CN)_2$
Fluoride	ZnF_2
Hydrosulfite	$ZnS_2O_4.2H_2O$
Nitrate	$Zn(NO_3)_2.6H_2O$
Oxide	ZnO
Phosphate	$Zn_3(PO_4)_2$
Peroxide	ZnO_2

The solubility of zinc compounds varies greatly, as in the case for zinc oxide. Dissolution of zinc oxide in water forms various ionic species as Zn^{2+}, $ZnOH^+$, ZnO_2H^- and ZnO_2^{-2} which are in equilibrium with water for a certain temperature at a specific pH value (Goodwin, 2017).

Apart from compound of zinc with chromite, most of the zinc compounds are colorless. With the help of colorless nature of zinc compounds they are utilized for films, plastics, rubber, cosmetics. In addition, zinc oxide, zinc sulfide and relative compounds may gain luminescence when they exposed to several types of radiation at different temperatures. With the help of this luminescence quality of its compounds, they can emit color light. In addition to that, compounds of zinc and phosphors could be obtained in variety of colors so opportunity to use it in television tubes and luminescent glass has arisen (Goodwin, 2017).

2.3. Processing Methods

Lead and zinc are the most abundant and commonly utilized base metals both for daily life and industrial applications with the consideration of their favorable properties and possibility to process by economically and technically feasible methods. Flotation is commonly used method in mineral and mining industries to achieve selective separation of economically valuable minerals or solids from raw material by using natural and induce differences of surface properties between particles (Wills, 1979). This process is applied both in larger and small scales for beneficiation of common metals as copper, lead, zinc cobalt, nickel whether in sulfide, oxide or carbonates minerals of these metals by using different chemical reagents to control different surface properties of minerals (Leja, 2004). The main motivation of flotation is to obtain mineral concentrate with high metallurgical grade and recovery values from low grade and complex ores in economically and technically feasible way. The froth flotation processing method first developed in the beginning of 20th century for beneficiation and concentration of sulfide type minerals than after improved to apply on non-sulfide mineral types. In addition to that, in recent years it has been started to use for nonmineral application as waste water treatment, deinking paper for recycling and recovery of industrial wastes (Leja, 2004).

At the present time, in order to obtain concentrate from non-ferrous minerals pyrometallurgical and hydrometallurgical methods are used. Pyrometallurgical process involves smelting of the ore at high temperatures in order to convert the mineral in oxide form. Anthracite is used as source of carbon to reduce minerals into oxide form in furnaces heated with natural gas or electricity. Pyrometallurgical processes require high temperature in order to construct effective reaction atmosphere which sometimes may exceed boiling points of the metals so metals needed to be collected in vapor stage. Due to indicated and similar reasons as high energy consumption, high capital investment and production of harmful gases; extraction of metals by using pyrometallurgical processes is not economically feasible and environmentally friendly. Because of these shortcomings; hydrometallurgical processes are more in use in order to extract valuable minerals from concentrates comes from pre-concentration processes or from run of mine (Abkhoshk et al., 2013).

Hydrometallurgical processes, namely leaching refers to dissolution of material in specific chemical solvent at certain operation parameters as temperature, pressure, solid-liquid ratio, duration, solvent concentration, pH and type of solvent. Even if hydrometallurgical treatment of ores is not as common as flotation, it has various has various important advantages as compared to pyrometallurgical process. Hydrometallurgical process is more attractive economically, environmentally, and technically. It brings less harm to environment due to it does not emit other hazardous gases like SO_2. In addition, metals can be obtained directly from leach solution in pure form or recovered from leach solution. A lot of factors make leaching preferable to high temperature smelting which are low temperature processing, low handling cost of leaching products and possibility of treatment of low grade ores (Abkhoshk et al., 2013).

2.3.1. Froth Flotation

Froth flotation is considered to be the most widely used method for the ore beneficiation. Flotation is the process in which valuable minerals are selectively separated from gangue material or other valuable minerals by using the differences in their physico-chemical surface properties (Vidyadhar & Singh, 2007). Briefly, froth flotation is a separation and also beneficiation process that takes the advantage of natural and induced differences in the surface properties of the minerals, whether the surface is readily wetted by water, namely hydrophilic, or repels water, that is hydrophobic (Wills, 2016). In other words, hydrophobicity of a solid present its ability to repel water and accrete to a gas bubble obtaining a solid-air assemble which is lighter than water and floating up to the surface of the liquid media. At the same time, hydrophilic materials have affinity to water and they do not accrete to the bubbles and fall down to the bottom of the flotation cell (Drzymala, 2007).

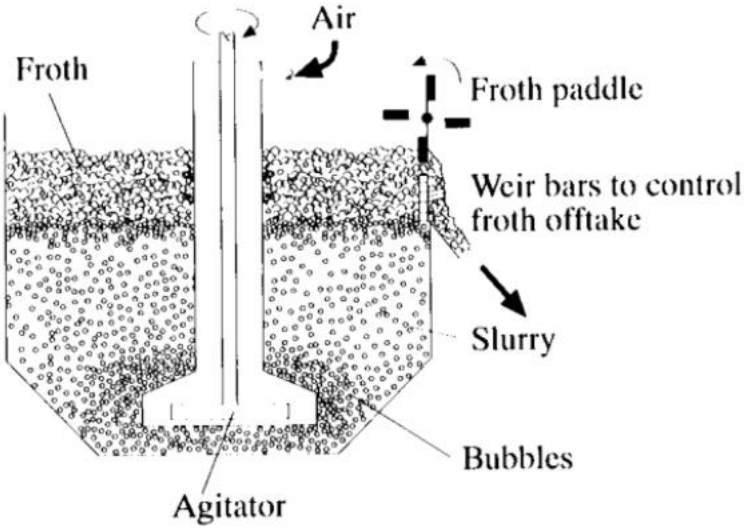


Figure 2.3Schematic Representation of a Conventional Flotation Cell (tank) (Wills B. A., 2016)

Within the scope of the theory of the flotation, hydrophobicity of the material shows the differences according to contact angel which represent angle between a particle, water and gas which are namely tangent to the solid-gas, gas-water and solid-water interfaces. Generally, contact angle is defined and indicated as the angle between gas and solid phases through water phase. At the same time, it can also be expressed as the contact angle between solid and water through the gas phases (Drzymala, 2007).

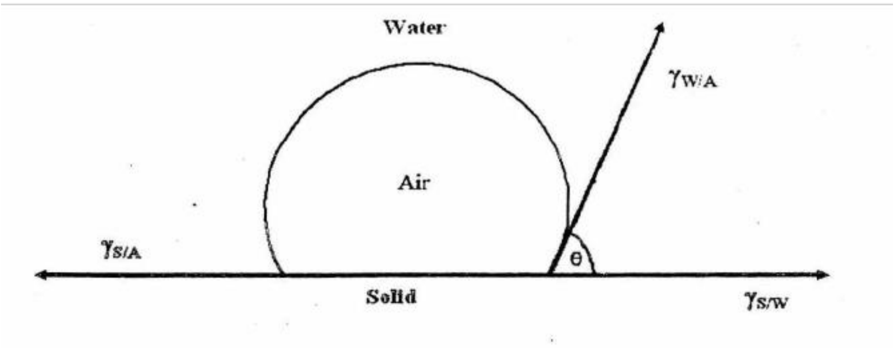


Figure 2.4 Representation of the Contact Angle between and Particle in an Aqueous Medium (Vidyadhar & Singh, 2007)

Surface energies between solid-air ($\Upsilon_{S/A}$) solid-water ($\Upsilon_{S/W}$) and water-air ($\Upsilon_{W/A}$) with respect to contact angle (θ) between mineral surface and bubble are represented in Figure 2.7. Floatability of a mineral increases through gaining higher affinity for air than for water under favor of high contact angle, by providing greater work of adhesion between particle and bubble interactions and thus the system is getting more resilient against disruptive forces (Vidyadhar & Singh, 2007). The force that is required to distort solid-bubble interface is named as 'the work of adhesion' ($W_{s/A}$) which is also equal to the work needed to separate the particle-air interface and to separate air-liquid and particle-water interfaces,

$$W_{s/A} = \Upsilon_{w/A} + \Upsilon_{s/w} - \Upsilon_{s/A}$$

Which results with following equation;

$$W_{s/A} = \Upsilon_{W/A}\,(1-\cos\theta)$$

It could be understood that, the greater the contact angle the greater is the work of adhesion between particle and air bubble interface and the more resistive the system against to destructive forces. The ability to float of a particle greatly enhancing with the increasing contact angle. In this context, minerals that have greater contact angle defined as aerophilic which means present higher affinity to air than water. (Drzymala, 2007). Generally, for decreasing the water repellency of the naturally hydrophobic minerals their affinity to water is reduced by the flotation reagents. In this context, the most important reagents are the collectors which adsorb on particle surface. In addition, the frothers are already used for supporting the formation of stable froth phase. Regulators, as activators, depressants and pH regulators which are used to provide optimum media for mineral to attach the air-bubbles and control the pH of the system by providing the suitable conditions with respect to the charge of the mineral surfaces (Vidyadhar & Singh, 2007).

2.3.1.1. Flotation Reagents

In the context of making a proper flotation work, separation depends on the range of chemical reagents added to the system to control the surface behavior of minerals in the feed material (Fuerstenau et al., 2007). The surface behaviors of different minerals are controlled by different types of reagents, in which each of them have a specific function (Rao et al., 2004). By this way, selectivity of the flotation work is achieved by using different types of reagents like; collectors, frothers, pH regulators, activators and depressants.

2.3.1.1.1. Collectors

The main aim of the collectors is to selectively form a hydrophobic layer on a specific mineral surface in the pulp that provide conditions for the attachment of the hydrophobic particles to air bubbles and recovery of these minerals in the froth phase. Basically, collectors would be defined as organic chemical materials that classified according to their molecular structures and would be categorized accordingly as non-polar group (non-ionizing) and polar group (ionizing) (Bulatovic, 2007). In this context, non-ionizing collectors are insoluble and strongly hydrophobic, such as kerosene. Then, non-ionizing collectors are utilized for naturally hydrophobic minerals such as coal and molybdenite to enhance their hydrophobicity and increasing the mineral – air bubble interactions (Laskowski & Raltson, 1992). Apart from that, ionizing collectors which are soluble and more commonly used type of collectors, having variety of utilization areas. These type of collectors are heteropolar that including a non-polar hydrocarbon group (hydro carbon chain, R) and a polar group in the form of different types. The non-polar hydrocarbon group has water repellency and providing hydrophobicity to the mineral surface. In addition, ionizing group provides solubility to the particle. In details, polar group would be defined as functional (or reactive) part and this part is adsorbed by the mineral surface. Based on this adsorption, non-polar part of the group moves toward to water, thus providing hydrophobicity. Polar or ionizing type of collectors would be categorized according to type of ion whether as anionic or cationic and they would be categorized according to target mineral types as non-sulfide or sulfide (Wills B. A., 2016). Anionic collectors are divided into two main group according to structure of polar group as sulfhydryl type and oxyhydryl type. The term sulfhydryl presents the SH group occur in the un-eroded from of the collector. The thiol term refers to the carbon that is bonded to the SH which are C-SH or R-SH. Sulfhydryl and thiol terms are used for these types of collectors which are utilized for the flotation of sulfide type minerals. Second type of anionic collectors is oxyhydryl type that presenting OH group, are commonly used for the flotation of non-sulfide minerals. Hydrocarbon chain length is generally longer than sulfhydryl collectors (Wills B. A., 2016; Leja, 2004)

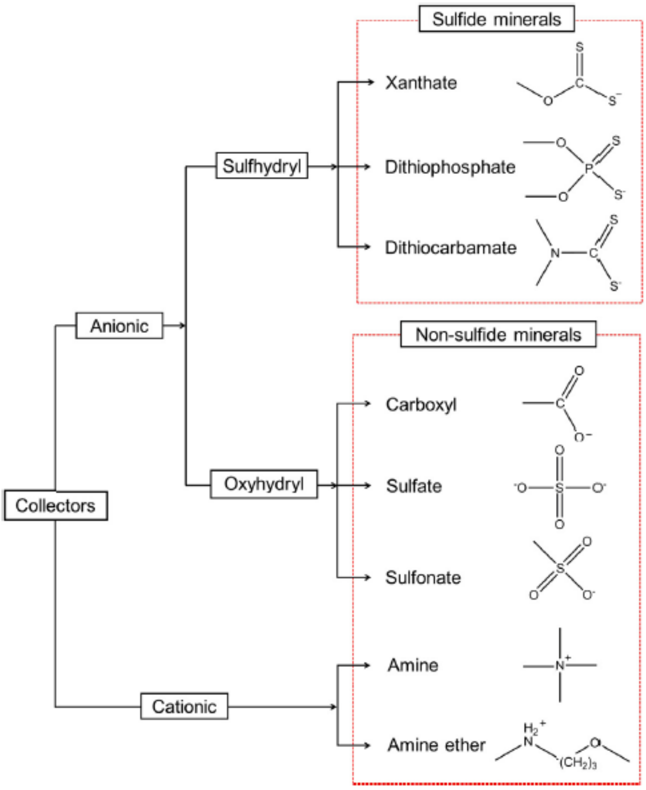


Figure 2.5 Classification of Ionizing Collectors (Wills B. A., 2016)

Moreover, other types of collectors are amphoteric reagents and chelating reagents. Amphoteric collectors would play the role of cationic and anionic type according to the various pH value. They are commonly used for the beneficiation of sedimentary phosphate deposits and to increase the selectivity of cassiterite flotation. Chelating reagents are preferred due to their capability to form stable compounds with selected cations (Wills B. A., 2016; Rao, 2004).

In most of the cases, collectors should be used in small amounts in order to improve selectivity. In the case of usage in excessive amounts, collector would form compound with other minerals rather than targeted group. In addition, it is hard to eliminate the adsorbed collector and thus the over dosing of the collector utilization would resulted with decrease in froth stability (Wills B. A., 2016).

2.3.1.1.1. Frothers

Basically, frothers would be defined as heteropolar surface active chemical compounds including polar groups of OH, COOH, C=O, OSO_2 and SO_2OH and a hydrocarbon radical which having the ability of adsorbing in the water-air interface (Bulatovic, 2007). The frothers are oriented in the air-water interface in a way that hydrophilic group placed toward to water while hydrophobic or non-polar group oriented toward to air phase (Khoshdast, 2011).

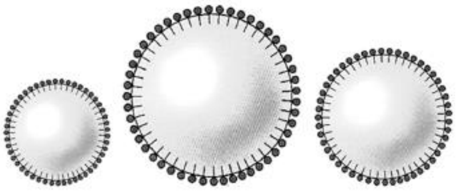


Figure 2.6 Orientation of the Frother Molecules in the Surface of Bubbles (Khoshdast, 2011)

There are three main functions of frothers in the flotation mechanism which are indicated below;

- Formation of small bubbles
- Decreasing bubble rise velocity
- Formation of stable froths (Wills B. A., 2016).

There are variety of different categorizations for the frothers according to their properties and behaviors in pulp solutions (Khoshdast, 2011). The most basic frothers are aliphatic normal alcohols such as pentanol and hexanol which have also decreasing the water solubility with increasing molecular weight. In addition to that, solubility of alcohol enhances in the case of additional oxygen atom. Methyl isobutyl carbinol (MIBC) in the group of branched frothers are used commonly in the industry. Moreover; long chained amines, sulfonates, sulfates and fatty acids would be examples of frothers which also behaves as and support the role of collectors. Generally these type of frothers utilized in flotation of non-sulfide ores (Drzymala, 2007).

2.3.1.1.2. Activators

Activators are used to support or enhance flotation in the presence of collectors. Interaction of the activator with the collector is one of the most important factor to perform the flotation work properly. Generally cations of hydrolyzing multivalent metal ions are used as an activators. Fe^{2+}, Fe^{3+}, Al^{2+}, Pb^{2+}, Mn^{2+},Mg^{2+}, Ca^{2+} would be example of metal ions used as activator. In addition to that, some of the anions also used as activator especially as fluoride and sulfide ions (Leja, 2004).

Oxidized minerals of lead and zinc as cerussite and smithsonite have lower capability to float with sulfhydryl collectors comparing to their sulfide counter parts due to combination of collector loss through precipitation by heavy metal ions dissolved from the mineral lattice and also because of the collector coatings weakly stucked and already removed by particle abrasion. These minerals are activated by using sodium sulfide or sodium hydrosulfide. This process is called as sulfidization. In some cases large amount of sulfidizer would be required because of the relatively higher solubility and water affinity of oxidized minerals. Dissociation of sodium sulfide is given in the below step by step:

$$Na_2S + 2H_2O \leftrightarrow 2NaOH + H_2S$$

$$NaOH \leftrightarrow Na^+ + OH^-$$

$$H_2S \leftrightarrow H^+ + HS^-$$

$$HS^- \leftrightarrow H^+ + S^{2-}$$

As it can be seen in the dissociation equations of sodium sulfide, releasing OH^-, S^{2-} and HS^- ions into the solution which would react with the mineral to modify its surface. With the help of sulfidization, sulfur ions pass into the mineral lattice and provide them relatively less soluble surfaces (Wills B. A., 2016).

2.3.1.1.3. Depressant

Depressants are used to enhance selectivity of flotation by making certain minerals hydrophilic so they have less capability to float (Wills B. A., 2016). The selectivity is achieved by depressing a group of mineral while minerals required to be floated, stay constant without any change, as not affected by them. Depressants would be inorganic, organic, acid, salt, base, redox and complexing reagents. Depressants would also be divided into three main group according to their working mechanism as;

- Removing collector from the mineral surfaces
- Changing the chemical composition of the mineral surfaces
- Dissociation of the collector (Drzymala, 2007).

In addition to that, several types of depressant used as dispersant which supply better condition for selective flotation than the system where the particles are aggregated. The most commonly used reagent as a dispersant is sodium silicate which restores high negative charge to generate electrostatic repulsion between particles, accomplished through a combination of adsorption of silicate anion and removal of metal cations from the surface (Wills B.A., 2016).

2.3.1.1.4. pH Regulator

The main aim of the pH regulators is to arrange the ionic composition of the pulp by changing the hydrogen ion concentration in the cell. With the help of the pH regulators, interaction between collector and desired mineral would be enhanced while interaction between collector and gangue mineral decreases (Bulatovic, 2007).

Most of the flotation processes performed under the alkaline media by taking the advantages of different types of collectors which perform better by staying stable in alkaline conditions. In addition alkaline media prevent the corrosion of flotation cells and pipes. Alkalinity would be provided by using some pH regulators as lime, sodium carbonate (soda ash), sodium hydroxide (caustic soda) and ammonia. Apart from that, in some cases acidic condition would be required in some flotation processes. For these types of cases, sulfuric or sulfurous acids would be preferred in order to obtain acidic media for flotation. Also, injection of exhaust CO_2 also could be preferred to obtain sufficient acidity (Wills B. A., 2016).

2.3.2. Flotation of Oxide Lead Minerals

As was aforementioned, chief mineral of lead metal is galena but due to gradual decrease in natural lead sulfide ore deposits lead oxide minerals have gained significant importance. As a typical lead oxide mineral cerussite would be alternative source of lead metal to meet future demand of the industry (Qicheng Feng, 2015). However lead oxide minerals are more difficult to float than their sulfide counter parts by using conventional flotation concentration methods and excessive reagent consumption due to higher solubility of oxide minerals and extensive hydration of oxide surfaces (Fuerstenau et al., 1986). Solubility of cerussite and galena are 1.1×10^{-13} and 8.3×10^{-29} respectively. Firstly, dissolved lead ions in the solution react with xanthate ions leading the formation of insoluble salts (Pb-alkyl xanthate) which results with larger reagent consumption. As a result of reaction between xanthate ions and carbonate ions, lead xanthate formed and carbonate ions releases into the solution therefore, a surface adsorption cannot be developed on the cerussite surface which removes important number of surface mineral layers (Popov & Vucinic, 1992). There are two general procedures known to develop technically and economically successful flotation beneficiation method for lead oxide minerals.

1- Utilization of fatty acids as collectors (Rao, 2004)
2- Utilization of sulfidizing agent to improve mineral's hydrophobicity (Feng et al., 2015).

The first method is not preferable due to its low selectivity and application possibilities are very limited. Usage of fatty acids would lead to activation of undesirable gangue minerals which results with low selectivity (Rao, 2004). The most generally used method for beneficiation of oxide lead minerals is sulfidization flotation which provides similar surface properties of sulfide minerals for oxide minerals and therefore oxide type minerals would be beneficiated by using xanthate type collectors (Qicheng Feng, 2015). In addition to that, most of the time ore is pretreated with the help of desliming process, especially if the ore include iron hydroxide minerals and clay minerals (Bulatovic, 2007).

Sulfidization is the most critical and sensitive procedure in flotation of oxide minerals. There are three critical factors effecting the performance and influence of sulfidization flotation as;

- Amount of sulfidizing agent
- The number of sulfidization steps
- Conditioning time of sulphidizer (Bulatovic, 2007)

The most critical factor is dosage of sulfidizing agent in a controlled manner. In this context, excess amount of sulfidizing agent results with depression of oxide minerals, while insufficient amount of sulfidizing agent causes ineffective sulfidization, so resulted with poor floatability of oxide minerals (Qicheng Feng, 2015). Addition of excess amount sulphidizer causes several negative effects on the flotation of oxide minerals. Firstly, since sulfidizing agents are strong reducing chemicals they would decrease the potential of mineral surfaces interface below the required value to form stable metal xanthate. Secondly, if sulfide ions completely adsorbed on the mineral surfaces, formation of metal sulfide becomes easier than formation of metal xanthate. In addition, since sulfide is less soluble than metal xanthate, metal xanthate formed on the mineral surface would be replaced by sulfide ions. Moreover, using excess amount of sulphidizer results with strongly negative mineral surfaces that prevent the adsorption of negatively charged xanthate ions on the mineral surfaces (Feng et al., 2015). As a last comment on effectiveness of sulfidization process, especially for mixed type sulfide-oxide lead minerals aeration would be important parameter. It was indicated that, in the case of lock of aeration floatability of the mineral rapidly decreases which causes low recovery of lead minerals (Bulatovic, 2007). As another important factor on the successof flotation of oxide minerals, according to type of impurities the number of sulfidization steps would be issue and positive effect of variety in stage additions of sulphidizer have been testified (Bulatovic, 2007).

Commonly used sulphidizers are Na_2S and NaHS for the flotation of oxide lead minerals. Prevention of Na_2S and NaHS depends on gangue mineral composition and whether anglesite or cerussite is beneficiated. In anglesite flotation NaHS is more preferable (Bulatovic, 2007). Sodium sulfide is most commonly used sulfidizing agent to convert oxide lead mineral surfaces into lead sulfide mineral surfaces so cerussite gain the ability to behave similar with galena during xanthate flotation (Qicheng et al., 2015).

As a fact that the metallurgical performance of the flotation concentration work is directly related to the sulfidization process, basically the amount of sulfide addition. In the case of excessive and deficient amount of sulfide additions, metallurgical performances were generally indicated under the desired grade and efficiency values. In more details, due to the dissolved lead contained in the flotation pulp, sulfides were consumed and precipitated as lead sulfide in the case of low sulfide additions. Similarly, excessive amount of sulfide additions caused to the depression of lead minerals mainly due to the shift of the oxidation-reduction potential of the pulp to the reducing conditions (Herrera-Urbina et al., 1999). Based on the fundamental theory of the sulfidization of cerussite entities, it was determined that lead sulfide, lead disulfide and lead polysulfide species were formed on the surface of the cerussite as the result of the effect of the addition of sulfidizing agent, namely Na_2S (Qicheng Feng, 2015). Basic reaction between cerussite and sodium sulfide might be presented as the following;

$$PbCO_3 + Na_2S \leftrightarrow PbS + Na_2CO_3$$

Moreover, as in the case of the flotation of cerussite, flotation of anglesite, namely lead sulfate, was indicated as challenging in terms of metallurgical grade and recovery values. For this reason, sulfidization of anglesite was also played an important role during the flotation concentration work. In this context, lead sulfate could not be activated in the case of lower sodium sulfide additions, while xanthate ions were substituted with the sulfide ions for the higher sodium sulfide additions, by causing the targeted lead entities to depress (Rashchi et al., 2005).

$$PbX_2 + S^{-2} \leftrightarrow PbS + 2X^-$$

Based on the challenging behavior of cerussite during the flotation concentration work, it was mentioned that the sulfidization is the most crucial process. Correspondingly, performance of the sulfidization was also played an important role for the metallurgical performance of the flotation work. Within this scope, based on the previous studies, it was indicated that the addition of sodium chloride will further improved the performance and effectivity of sulfidization process. Briefly, the main mechanism for the increased sulfidization performance was the compression of cerussite electrical double layers in the presence of sodium chloride in which increased convenience of cerussite surfaces led to the great adsorption of sulfide ions (Liu et al., 2019; Feng Q. et al., 2016). In other words, based on the zeta potential measurements on sodium chloride pretreated cerussite including ore, it was seen that the pretreatment caused to increase in zeta potential thereby active sites on cerussite surfaces increased. In details, it was a known fact that one of the main challenge during the cerussite flotation was the dissolution of lead ions in aqueous phase, contrary to this dissolved lead ions were directly migrated from aqueous solutions to the mineral surface as the result of the sodium chloride pretreatment and thus led to the further improvement in hydrophobicity of the mineral surfaces (Feng Q et al., 2015). Considering all of these effects of sodium chloride pretreatment, it was determined that the aforementioned process directly increases the flotation recovery of cerussite in significant amounts. In this context, according to the previous studies on the pretreatment of cerussite containing ore with sodium chloride, it was determined that flotation recovery of cerussite was increased from 50 % to 70 % at pH values around 9 (Liu et al., 2019). Apart from that, flotation recovery of cerussite was increased between 16.63 % and 10.51 % as the result of the pretreatment with different amounts of sodium chloride (Feng Q. et al., 2015).

In ındustrial scale, application type of collector used for flotation of oxide minerals is limited with xanthate while dithiophosphates and merceptants are utilized as secondary collectors resulting from contamination of naturally hydrophobic impurities in the ore which makes utilization of anionic type collector inapplicable. Utilization of chelating agents as collector in oxide lead mineral flotation has been tried, despite the fact that they results with good recovery and grade values in laboratory scale, these collectors are not feasible in industrial scale applications (Bulatovic, 2007).

One of the other important parameter that directly affects the flotation performance of cerussite is the pH value of the pulp. In this context, it was determined that higher flotation recoveries could be obtained in the case of acidic pulp conditions with respect to its alkaline counterparts (Feng Q. et al., 2016; Rashchi et al., 2005). The major mechanism for the effect of pH is based on the distribution of sodium sulfide in flotation pulp with respect to the different pH values. Basically, HS^- entities are the dominant species in the case of higher pH values, namely in alkaline conditions. In details, excess amount of sulfide ions prevents the interaction between sulfidized cerussite and collector entities and also exclude the adsorption of xanthate collectors on the sulfidized cerussite mineral surfaces. On the other hand, cerussite entities were depressed at pH values above 11 due to the formation of the stable lead hydroxyl species, as Plumbite. At that conditions, OH^- ions were directed through the lead sulfide surfaces, thereby decreasing the effect of sulfidization and cerussite – collector interactions. This reaction mechanism could be basically presented as the following (Feng Q. et al., 2016);

$$PbS + OH^- \leftrightarrow Pb(OH)^+ + S^{2-}$$

$$PbS + 2OH^- \leftrightarrow Pb(OH)_{2aq}^+ + S^{2-}$$

$$PbS + 3OH^- \leftrightarrow Pb(OH)^{3-} + S^{2-}$$

$$Pb(OH)_{2aq}^- \leftrightarrow Pb(OH)_{2solid} + S^{2-}$$

As was mentioned, formed lead hydroxyl species were generally hydrophilic in which directly decreased the flotation concentration performance in terms of lead recovery. In consideration of all these, it was determined that sulfidization process and also the sulfidized surface of cerussite was more stable at acidic conditions, thereby the performance of the conducted flotation concentration work would be higher in the case of slightly acidic or acidic pulp conditions (Feng Q et al., 2016).

Based on the previous works on the flotation of cerussite containing ore materials, it was indicated that the flotation recovery of lead entities would be directly affected by type of collector, dosage of collector, pH of the pulp, type of the sulfidization agent and dosage of the sulfidization agent. In this context, it was seen that a concentrate that contains 41.32 % Pb was obtained from zinc leach residue, including cerussite and anglesite, by the addition of 7000 g/t sodium sulfide in the presence of xanthate, namely potassium amyl xanthate, as the major collector (Rashchi et al., 2005). On the other hand, based on the previous flotation work on oxide lead-zinc ore from Adana, Aladag region of Turkey, a lead concentrate that contains 65.42 % Pb was obtained with 77 % Pb recovery from a feed material that contains 10.17 % Pb, as the result of the six stage flotation concentration work. At this stage, 350 g/t KAX, 250 g/t Aero407 (Mercapto Benzo-thiazole) were used as the main collectors and 4500 g/t Na_2S was added as the sulfidizing agent. Apart from that, it was seen that zinc sulfate, which would be used for the depression of zinc oxide entities, had no effect on the flotation performance of the cerussite entities (Önal, et al., 2005). In the context of the previous flotation concentration works on oxide lead-zinc ore samples, it was indicated that a lead concentrate that contains 70.70 % Pb was obtained with 74.70 % Pb recovery from a feed material that contains 6.69 % Pb as cerussite entities. It was also noted that the major gangue minerals were determined as calcite, dolomite and quartz and the whole mineral surfaces were covered with the limonite entities. In addition, importance of sulfidization was emphasized within the scope of the aforementioned study that the addition of sodium sulfide directly affected the flotation recovery of cerussite entities (Senturk, Atalay, & Ozbayoglu, 1993).

2.3.3. Hydrometallurgical Methods

Hydrometallurgy is the major aqueous methods for the extraction of metallic elements or valuable entities from the corresponding metallic ores (Free, 2013). Briefly, the term hydrometallurgy is composed of the term ‘hydro’ which means water and the term ‘metallurgy’ that inferred the production of metallic entities (Havlik, 2008).

During early ages, it was believed that people used furnaces and fire in order to melt the materials and extract valuable metallic content. Later on, they hade started to use the water and the aqueous solutions instead of dry and high temperature methods in order to process the ores including valuable metallic entities. History of today’s context of hydrometallurgy dates back to the end of 19th century. Hydrometallurgy would be basically conceivable as production of metals, metal salts or any other metal compounds by using chemical reactions occurred with the help of the aqueous and the organic solutions. Most of the time hydrometallurgical processes performed under the pressure, which changes between few kilopascal and 5000kPa and in the temperature range varying from 25°C to 250°C (Mukherjee & Gupta, 1990).

There are several advantages of hydrometallurgical processes as indicated below;

- Hydrometallurgical processes are more flexible for the treatment of complex ores and for the production of different types of by-products, namely for full processing of the ore materials in order to evaluate the whole valuable content.
- Hydrometallurgical processes provide opportunity to processes complex ores.
- Labor requirement is generally less in hydrometallurgical plants
- Hydrometallurgical processes would be generally performed for low grade ores
- It is possible to separate closely related metals
- Particularly with respect to pyrometallurgical methods hydrometallurgical processes requires less energy
- Solution and slurries produced or used with in the hydrometallurgical plants would be easily transferred by using closed pipeline systems (Mukherjee & Gupta, 1990).

Generally, metal extraction is called as leaching which would be divided into different types of methods as in-situ leaching, heap leaching, dump leaching, vat leaching and agitated leaching. In addition to that utilized chemicals, namely leaching reagents would be varied according to type of the ore to be processed.

2.3.3.1. Agitated Leaching

Agitation leaching is applied for wide range of mineral types and utilized for over 200 years (Marsden & House, 2006). This method is generally performed by using agitated vessels and the materials are dispersed in the solution via the help of the injected gas or a rotating impeller. Material dissolution is provided by batch basis or continuous basis. The ore-liquid mixture passes through vessel to vessel in series rather than dissolution in a single vessel in order to obtain maximum extraction ratio. There are two significant differences between agitated leaching and percolation leaching types. The first difference is solution continuous phase in agitating leaching. In addition, while turbulent flow is provided by agitated leaching, laminar flow is commonly obtained in the percolation. Due to the differences between these two methods, there are significant differences in obtained mass transfer. Higher mass transfer is achieved under turbulent conditions (Mukherjee & Gupta, 1990).

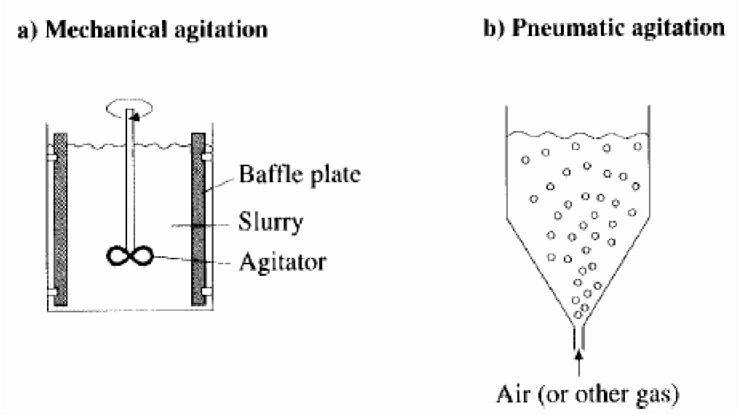


Figure 2.7Agitation Leaching (Hoşten, 2019)

There are several factors which effects the leaching performance of agitated leaching directly. The first and the foremost parameter is particle size of the material. Within this scope, leaching performance increases with the decreasing particle size. In addition, it is hard to keep coarse particles in suspension. Second significant parameter affecting the leaching performance is slurry density. Mass transfer reaches maximum rates at lower slurry densities. However at the same time, retention time of the material increases at higher slurry densities resulting with the extension in exposure time of the material with solvent liquid. The other parameter which influence the leaching performance is the retention time. Determination of optimum retention time depends on the mineral characteristic and should be adjusted according to performed test work (Marsden & House, 2006).

2.3.3.2. Leaching Reagents

In order to construct a successful leaching operation which resulted with maximum metal extraction rates in an economically feasible way, reagent choice should be made in a controlled manner. There are variety of leaching reagents and selection was made depending on the type of targeted mineral and economics of the operation. The basic required properties of the leaching reagent should be considered before design of the commercial leaching plants. Leaching reagents should be economically and technically available and possibility to regenerate would be advantageous. In addition, leaching reagent should have ability to dissolve targeted metal without presenting any affinity to gangue entities (Hoşten, 2019). Leaching reagents are classified according to their chemical nature.

Table 2.6Classification of Leaching Reagents (Mukherjee & Gupta, 1990)

Category	Reagent	Targeted Minerals
Acids	Dilute H2SO4	Copper Oxide, Zinc Oxide
	Dilute H2SO4 + oxidant	Sulfides of Cu, Ni, and Zn; uranium oxide ores
	Concentrated H2SO4	Copper sulfide concentrate, Laterites
	Nitric Acid	Sulfides of Cu, Ni, and Mo, Mo scrap, Uranium concentrates, Zirconium oxide
	Hydrochloric Acid	Ilmenite, nickel matte, reduced cassiterite
	Hydrofluoric Acid	Columbite-tantalite ore
Alkalies	Sodium Hydroxide	Bauxite
	Sodium Carbonate	Uranium Oxide, Scheelite

	Ammonium Hydroxide + Air	Nickel sulfide, Copper Sulfide, Reduced laterite
Salts	Ferric Chloride/ sulfate	Base Metal Sulfide Concentrates
	Cupric Chloride	Base Metal Sulfide Concentrates
	Sodium or Potassium Cyanide + Air	Gold and Silver Minerals
	Ferrous Chloride + Air	Nickel Sulfide
Aqueous Chlorine	Aqueous Chlorine, Hypochlorous Acid, Hypochlorite	Sulfide Concentrates of Cu, Ni, Zn, Pb, Hg and Mo and reduced laterite
Water	Water	Sulfates and chlorides, sodium vanadate, -molybdate, -tungstate, -stannate

Table 2.5 presents the summary of the classification of commonly used leaching reagents. Water, as the most basic solvent preferred if the targeted mineral is water soluble or they have pre-treated and transferred in to the water soluble form (Hoşten, 2019). Acid leaching of the mineral is the most wide spread method in terms of economics and technical availability. However, acidic leaching reagents were used if only if the gangue minerals are not acid consuming (Mukherjee & Gupta, 1990). In the case of existence of acid consuming gangue minerals within the ore material, alkaline leaching reagents would be preferred. Alkaline reagents are more selective and less corrosive by comparing with the acidic reagents (Hoşten, 2019). Salts are used as leaching reagents if the leaching operation contains sulfidic resources and also salts would be strength solvents for gold and silver in the presence of oxygen (Mukherjee & Gupta, 1990).

2.4. Processing of Zinc Oxide Minerals

Although the beneficiation and the processing methods of zinc sulfide minerals are economically and technically feasible by using conventional methods, due to decrease in zinc sulfide reserve through all over the world, requirement to develop alternative feasible methods for the beneficiation of zinc oxide minerals has been raised to meet the future demand of zinc metal. Zinc oxide is a general term including variety of minerals but only few of them have economic value. These aforementioned minerals are smithsonite, hydrozincite and zinc silicates hemimorphite and willemite (Abkhoshk et al., 2013).

Beneficiation of oxide zinc minerals by using conventional flotation method is relatively more difficult than flotation of their sulfide counterparts because of higher solubility and extensive surface hydration (Moradi & Monhemius, 2011). Sulfidation-flotation was utilized in order to obtain a concentrate enriched in zinc oxide minerals. Also, the sulfidization was tried to be provided by using different types of sulfidizing agents as sulfur dioxide, sulfide ions and/or metabisulfide ions. With the help of these ions possibility to treat zinc oxide minerals by using sulfide collectors has raised. However these methods were not commonly used in the industry due to several disadvantages as excessive reagent consumption and low recovery values. In addition, sulfidation-amination flotation would be applied however this process is also difficult to achieve because of the process was affected too much due to formation of slime entities which needs additional chemical pretreatment. Although desliming may increase the flotation efficiency it also resulted with significant amount of zinc loss (Wu et al., 2017). To sum up; treatment of zinc oxide minerals by using conventional flotation method have several shortcomings and some main ones are indicated below.

- Ultra-fine grinding would be required in order to provide sufficient liberation of particles (Moradi & Monhemius, 2011).
- Complex flotation design is needed including several recycling (Moradi & Monhemius, 2011).
- Flotation of zinc oxide minerals results with low Zn recovery value (Abkhoshk et al., 2104).
- Process is not economically feasible due to the excessive reagent consumptions (Abkhoshk et al., 2014).

Due to above concatenated reasons, at the present time zinc production is achieved by using two method namely pyrometallurgy and hydrometallurgy. As indicated before; pyrometallurgical processes including smelting of the ore at very high temperature. This process presents several disadvantages, such as large capital investments, high energy consumption and production of environmentally harmful gases. Although in the 1960s hydrometallurgical and pyrometallurgical methods had equal importance for zinc production, in today's word extractive metallurgy of zinc metal has gained great significance (Abkhoshk et al., 2013).

For the extraction of zinc from low grade zinc oxide ores, development of low energy consuming hydrometallurgical processes are required. Basically, leaching of zinc oxide minerals could be achieved by using different types of chemicals. Most commonly preferred leaching method for zinc extraction from oxide mineral is performed with acidic and alkaline media. In order to obtain acidic media most widely used chemical is H_2SO_4 which requires less operational cost. In addition, to construct alkali leaching of zinc oxide most widely used chemicals are ammonia and its derivatives. Alkali leaching provide less corrosive operation and easy solid-liquid separation processes (Chen, et al., 2009). In addition to these leaching reagents, there are variety of studies in the literature which are conducted by using different types of leaching reagents as organic acid (Hurşit, Laçin, Saraç, 2009) and boric acid (Abalı et al., 2014) in order to extract zinc from oxide minerals at reasonable grade and recovery values.

There are several factors affecting the leaching performance as reagent concentration, temperature, reaction time, solid/liquid ratio; particle size and stirring speed. Reagent concentration is one of the most significant factor which influence the leaching performance in terms of metallurgical grade and recovery values. Although the increasing reagent concentration results with the increase in leaching rate, high reagent concentration causes dissolution of gangue minerals and excessive reagent consumption. Moreover, temperature is also directly proportional to the leaching rate since the reaction rate increases as the temperature increases. As another factor particle size is also important for leaching performance. Decreasing particle size accelerates the reaction rate with the increasing surface area available for the reaction. In addition, solid/liquid ratio affects reaction rate inversely proportional so decreasing solid-liquid ratio enhance the leaching performance. Finally, as the least significant parameter, increasing stirring speed results with the increase in reaction rate however, above the certain rate it doesn’t affect the leaching performance (Abkhoshk E. et al., 2013).

2.4.1. Acidic Leaching of Zinc Oxide

As the result of the decrease in high grade zinc oxide minerals, leaching methods to recover the low grade zinc oxide ores should be improved. Acidic leaching is favorable leaching method in terms of recovery and grade values of final products (Ntuli et al., 2011). Leaching of zinc oxide minerals in acidic media is one of the typical example of mass transfer reaction (Yoshida, 2003). During the leaching of zinc oxide in acidic media, the adsorption of protons onto the solid surface at the solid-liquid interface has a significant importance. Weaknesses between metal and oxygen bonds results with releasing metals protons into the solution (Lottering, 2016). Acidic conditions are favorable for dissolution of the metals. There are different types of chemicals utilized in acidic leaching of metals such as H_2SO_4, HCl and HNO_3. Sulphuric acid is the most widely preferred leaching reagent due to its chemical properties, availability and relatively lower cost (Ntuli et al., 2011). The dissolution reaction between zinc oxide and sulphuric acid occurs as following;

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$ (Mukherjee & Gupta, 1990)

Sulphuric acid is utilized in dilute conditions and stages for the extraction of zinc processes. This process is used commercially in industry by taking the technical and economic advantages of the method (Mukherjee & Gupta, 1990). Despite from the advantages of hydrometallurgical treatment of zinc oxide mineral by using sulphuric acid, the process has few disadvantages limiting its technical applicability. Depending on the impurity content of the ore, sulphuric acid leaching of low grade zinc oxide mineral would be expensive because of the difficulties in solid/liquid separation process. During the leaching operation by using sulphuric acid, impurities contained in the ore such as Co, Cd, Ni, Cu, Fe, As, Sn, Se, Ge Sb, Cl and F also dissolved which results with silica gel or other operational problems (Abkhoshk E. et al., 2013). Dissolution of impurities also cause excessive reagent consumption and complex purification process could be required. (Ma et al., 2011). In addition, disposal of H_2SO_4 is an also important issue and should be considered from an environmental point of view (Mukherjee & Gupta, 1990).

Since the sulphuric acid leaching is one of the most commonly used method for the extraction metallurgy of low grade zinc oxide ore, there are several studies that was conducted on sulfuric acid leaching. In order to evaluate the method more corporeally, it would be beneficial to mention few of them. Firstly, a study was conducted by Abdel-Aal using an ore sample which contains hemimorphite [$Zn_4Si_2O_7(OH)_2.H_2O$] and willemite [Zn_2SiO_4] as major minerals, as well as smithsonite [$ZnCO_3$], cerussite [$PbCO_3$], quartz [SiO_2], gypsum [$CaSO_4.H_2O$], and goethite [FeO(OH)] as minor minerals. The maximum extraction rate is obtained as 94% under the following conditions as 70°C temperature, 10% sulphuric acid concentration, 1:20 solid-liquid ratio, stirring speed of 550 rpm and the ore was leached for 180 min (Abdel-Aal, 2000). Apart from that, another study on sulphuric acid leaching of low grade zinc oxide mineral is conducted to evaluate the effect of different leaching methods as batch and semi-batch system. The ore sample used in the tests contains 61% of zinc oxide and remaining part is consist of oxides. The maximum extraction ratio is obtained as 91.2% under the following conditions; 70°C temperature, 6% sulphuric acid concentration, stirring speed of 530 rpm and the ore was leached for 180 min (Ntuli et al., 2011).

On the other hand, beside the sulphuric acid is the most commonly used acidic leaching reagent in extractive metallurgy of zinc oxide, boric acid also tried to be evaluated as an alternative lixiviate for the acidic leaching of zinc oxide since 0.2 teragrams of boric acid produced in Turkey per year. Briefly, the boric acid produced with the chemical formula of H_3BO_3 containing 56.25% B_2O_3 (Abalı et al., 2014). The dissolution of boric acid in aqueous medium occurs as following;

$B(OH)_{3(s)} + H_2O \rightarrow B(OH)_4{}^-{}_{(aq)} + H^+{}_{(aq)}$

The dissolution of smithsonite in boric acid is occurred as following;

$ZnCO_{3(s)} + 4B(OH)_4{}^-{}_{(aq)} + 4H^+{}_{(aq)} \rightarrow ZnB_4O_{7(s)} + CO_{2(g)} + 10H_2O_{(l)}$

Reaction between smithsonite and boric acid resulted with zinc borate which is utilized as fire retardant in industrial applications. Despite the fact that limited study has been performed on hydrometallurgical extraction of zinc from oxide zinc ore by utilizing boric acid leaching, there is a successful study on that topic. Within the scope of the study treated the ore that contains 37.74% ZnO, 19.46% PbO and 2.05%Fe_2O_3. The major mineral containing with in the ore sample are smithsonite ($ZnCO_3$), hydrozincite ($Zn_5(OH)_6(CO_3)_2$), cerussite ($PbCO_3$) and the minor minerals are hemimorphite ($Zn_4Si_2O_7(OH)_2H_2O$) and hematite (Fe_2O_3). There are several parameters investigated within the scope of boric acid leaching process of zinc oxide such as particle size, leaching time, temperature, stirring speed, boric acid concentration and solid-liquid ratio. The maximum extraction rate of zinc is obtained as 94.81% under the following condition as; 40°C temperature, 0.9 mol/L boric acid concentration, 1/100 solid-liquid ratio, stirring speed of 700 rpm and the ore was leached for 1 hour (Abalı et al., 2014).

2.4.2. Ammonia Leaching of Zinc Oxide

Ammonia is commonly utilized as an efficient leaching reagent in extractive metallurgy of non-ferrous metals. The application technology of ammonia leaching process improved from traditional treatments of copper to the extractive metallurgy of zinc, cadmium, silver and gold (Meng & Han, 1996).

There are several reasons which cause expansion in utilization area of ammonia leaching. This process provides possibility to extract the valuable minerals from low grade ores and supply economically competitive operation possibility since the ammonia could be regenerated by the evaporation and set up cost is relatively lower with respect to other possible alternative leaching lixiviants (Liu et al., 2011). In addition to that, while the non-ferrous valuable metals have capability to form metal ammine complexation with ammonia, major gangue minerals such as Fe, Pb, Ca and Mg precipitate as hydroxides due to their poor complexation ability with ammonia (Ding et al., 2010). This provides selective extraction of targeted metals by leaving the gangue minerals within the leach residue (Ma et al., 2011). Moreover, precipitation of gangue minerals rather than dissolution, prevents the excessive leaching reagent consumption (Ding et al., 2010). Therefore; ammonia leaching is favorable process for treating the low grade zinc oxide ores with a high content of alkaline gangue (Liu et al., 2011).

Ammonia was used for different purposes since early history and first commercial production of ammonia was achieved in 1880. Hydrometallurgical process by using ammonia as leaching reagent was first applied for the extraction of copper from copper oxide mineral and native copper. The first industrially scaled application of ammonia leaching was constructed in 1916 for the metallurgical extraction of copper. The first statement on ammonia leaching of zinc was released as ‘The Schnabel Process’ in 1880 (Ding et al., 2010). In today’s world extractive metallurgy of non-ferrous metals such as zinc by using ammonia leaching is applied worldwide (Meng & Han, 1996).

Throughout the application of ammonia leaching of zinc metal, ammonia and/or ammonia salts such as ammonium carbonate, ammonium chloride can be used as leaching reagents. There are several studies conducted by using ammonium chloride. By briefly mentioning, ammonium chloride has been used by different researchers. Firstly, an ore sample containing 19.51% Zn and SiO_2, Fe, Al_2O_3, MgO and CaO as major gangues was used in extraction of zinc by using ammonium chloride. The maximum extraction rate was obtained as 92.1 % under following conditions as 80°C temperature, ammonia concentration 7.5 mol/L, 1:10 solid-liquid ratio and the ore was leached for 1 hour. (Rui-xiang, et al., 2008). The other study on ammonia chloride leaching of zinc oxide is conducted by using ore sample containing 30.28% Zn and

20.72% Al_2O_3 and 15.32% SiO_2 as major gangue minerals. The maximum extraction rate was obtained as 92.1 % under the following conditions as 90°C temperature, ammonium chloride concentration 5 mol/L, 1:10 solid-liquid ratio and the ore was leached for 4 hours (Ju et al., 2004). In addition to that, ammonia leaching of low grade zinc oxide mineral by using ammonia as leaching agent is studied and the maximum extraction rate of zinc has been obtained as 76.66%. Run of mine ore used for this study contains cerussite and smithsonite as the major minerals. Ore was pretreated by applying flotation beneficiation method in order to obtain cerussite concentrate. After that, flotation tailing containing smithsonite was exposed to ammonia leaching under the following conditions as 7M NH_3 and 12 hours of treatment (Talan et al., 2017). Moreover, as another ammonia salt, ammonium carbonate has been used to extract zinc from smithsonite and the maximum extraction rate was obtained as 86% under the following conditions as 7M ($(NH_4)_2CO_3$) and 12 hours of treatment (Talan et al., 2016).

2.4.3. Organic Acid Leaching of Zinc Oxide

Hydrometallurgical treatment of zinc oxide by acidic leaching and ammonia leaching are the most widely used methods. However, as indicated before acidic leaching of zinc oxide minerals especially for containing iron hydroxide minerals and carbonaceous impurities would be economically unfeasible due to dissolution of gangue minerals which also causes excessive reagent consumption and difficulty in solid-liquid separation. In addition to that, although the ammonia leaching is relatively more feasible method it would be resulted with low metal extraction rate especially in the treatment of low grade complex zinc silicate ores (Ai-yuan, et al., 2016). Due to these reasons; in addition to the utilization of inorganic acids, organic acid leaching of zinc oxide minerals has been gained importance in the extractive metallurgy of metals (Deng, et al., 2015). Organic acids are not commonly used leaching reagents because of their low dissolution capability however, they would be favorable due to easy biodegradation (Ghasemi & A.Azizi, 2017). Therefore, leaching by using organic acids would not cause environmental considerations (Park et al., 2013). Organic acids have been determined as effective reagents for the dissolution of heavy metals due to their ability to form stable chelate complexes with heavy metals such as copper, zinc and lead (Park et al., 2013). Citric acid, gluconic acid, acetic and lactic acid are the examples of organic acids that are used in order to hydrometallurgical treatment of metallic entities. From the development of alternative methods for the extraction of zinc oxide minerals point of view, dissolution of smithsonite by using gluconic acid (Hurşit et al., 2009) and leaching of low grade zinc ore by using citric acid (Ai-yuan, et al., 2016) has been studied. Organic acids in hydrometallurgical treatment of zinc oxide minerals supplies slightly acidic conditions (pH 3-5) (Ghasemi & A.Azizi, 2017).

According to data obtained from gluconic acid leaching tests of zinc oxide minerals, it was seen that significantly high extraction rates would be possible to achieve. Within the scope of the previous study performed by Hurşit, Laçin and Saraç, smithsonite with the chemical composition of 57.28% ZnO, 1.50% Al_2O_3, 1.80% SiO_2, 0.90% CaO, 1.60% Fe_2O_3 and 1.42% of impurities, taken from Kayseri, Turkey was used. Reaction between smithsonite and gluconic acid occur as following;

$$2HC_6H_{11}O_7 \leftrightarrow 2HC_6H_{11}O_7^-{}_{(aq)}$$

$$ZnCO_3 + 2H^+_{(aq)} \rightarrow Zn2^+_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

$$ZnCO_{3(s)} + 2HC_6H11O_{7(aq)} \rightarrow Zn_2^+{}_{(aq)} + 2C_6H_{11}O_7^-{}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

There are several parameters investigated within the scope of gluconic acid leaching process of zinc oxide such as particle size, leaching time, temperature, stirring speed, gluconic acid concentration and solid-liquid ratio. The maximum extraction rate of zinc was obtained as 99.63% under the following conditions as 70°C temperature, 1.25 mol/L gluconic acid concentration, 1/250 g/ml solid-liquid ratio, stirring speed of 62.80 rad/s and the ore was leached for 50 min (Hurşit et al., 2009). Although the extraction rate of the conducted tests was pretty high, test conditions doesn’t seem applicable industrially in economically feasible way since the leaching temperature was very high and solid-liquid ratio was extremely low.

Citric acid is one of the world’s largest-tonnage fermentation products (Demir et al., 2006). It is a weak organic acid and naturally contained in citrus fruits such as lemon and lime and certain berries (Shabani et al., 2012). Citric acid is found as the effective leaching reagent due to its ability to form soluble complexes and chelates with metal ions by taking the advantage of having low molecular weight. In addition, as a matter of fact it is thought to be more active than H_2SO_4 according to the ability of extracting metals or metal oxides with respect to their chemical activities. Therefore the utilization of citric acid in extraction metallurgy of zinc oxide minerals is preferable since it is highly available, cheap and environmentally friendly. The reaction between citric acid and smithsonite is occurs as following;

$$C_6H_8O_7 \leftrightarrow 2H^+ + C_6H_6O_7^{2-}$$

$$ZnCO_3 + 2H^+ \rightarrow Zn^{2+} + CO_2 + H_2O$$

$$ZnCO_3 + C_6H_8O_7 \rightarrow Zn^{2+} + C_6H_6O_7^{2-} + CO_2 + H_2O$$ (Irannajad, Meshkını, & Azadmehr, 2013)

Leaching of low grade zinc oxide minerals in NH_3-$H_3C_6H_5O_7$-H_2O was studied within the consideration of different parameters as temperature, citric acid concentration, ammonia concentration, leaching time, solid liquid ratio and stirring speed. Ore sample which is utilized within the scope of this study contains silica, calcium carbonate, lead carbonate and hemimorphite. Mineral composition of zinc includes hemimorphite, smithsonite, zinc sulfide, franklinite. The maximum zinc extraction rate was obtained as 82.1 % under the following conditions as 25°C temperature, 1 M citric acid concentration, 6 M ammonia concentration, 1:5 solid-liquid ratio, stirring speed of 300 rpm and the ore was leached for 1 hour (Ai-yuan, et al., 2016).

As another important study on extractive metallurgy of zinc by using citric acid was performed by Seyed Ghasemi, Seyed Mahyar and Azizi Asghar from Shahrood

University of Technology (Ghasemi et al., 2018). Within the scope of the study ore sample consists of zinc oxide and lead oxide minerals with grades of 5.91% and 5.32% respectively. Based on the mineralogical analysis of sample used during leach studies, main zinc mineral was identified as smithsonite ($ZnCO_3$) and main lead mineral is defined as cerussite ($PbCO_3$). Main gangue compositions are defined as 24.77% SiO_2, 15.68% Fe_2O_3, 15.42% CaO and 15.76% BaO. In addition to that, d_{80} of feed material used in leach experiments is less than 150 micron. Five experimental parameters as acid concentration, temperature, stirring speed, solid liquid ratio and leaching time were considered during leaching tests. The maximum zinc extraction ratio was achieved as 99.44% under the following conditions as 78°C temperature, 1M citric acid concentration, 413 rpm stirring speed, 20.61 ml/g liquid-solid ratio and sample was leached for approximately 81 min (Ghasemi et al., 2018).

Since organic acid leaching of metals from oxide mineral is becoming significant topic day by day there was need to arise for mentioning about one more successful study on citric acid leaching of zinc from low grade zinc oxide minerals. Citric acid leaching of low grade zinc oxide mineral has been studied by Mehdi Irannajad, Mohammed Meshkını and Amir Reza Azadmehr from Amirkabir University (Irennajad et al., 2012). The ore sample mainly consists of 16.1% ZnO, 8.0% Al_2O_3, 21.2% SiO_2, 21.3% CaO and 3.59% Fe_2O_3 was used within the scope of the study. Five experimental parameters as acid concentration, temperature, particle size, solid liquid ratio and leaching time were considered during leaching tests. The maximum zinc extraction ratio was achieved as 82% under the following conditions as 80°C temperature, 0.5M citric acid concentration, 350 micron particle size, and sample was leached for approximately 60 minute (Irennajad et al., 2012).

CHAPTER 3

MATERIAL METHOD

3.1. Materials

The ore samples used within the scope of this thesis study was taken from Yozgat - Akdagmadeni district of Turkey. The ore sample mainly consist of oxide lead and zinc minerals such as cerussite ($PbCO_3$), smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4) as major valuable minerals and goethite (FeOH), quartz (SiO_2), dolomite ($CaMg(CO_3)_2$), kaolinite ($Al_2Si_2O_5(OH)_4$) and lesser extent analcime ($NaAlSi_2O$) as gangue minerals. In this context, 200 kg of representative r.o.m sample was taken from the mine site, from the previously prepared 5x5 m. trenches, and delivered to the Middle East Technical University Mineral Processing Laboratory. In order to use in characterization studies and laboratory tests as feed sample, representative samples were prepared. Details about sampling, characterization studies and applied processing methods are given in the following subsections.

3.2. Methodology

The main motivation of the present thesis study is developing an optimum a mineral processing flow sheet for metallic minerals, as cerussite and zinc oxides, which also having economic value. In order to obtain cerussite concentrate, optimum flotation conditions were determined within the help of the detailed characterization studies. Thereafter, optimum leaching conditions by using different leaching reagents were determined in order to extract zinc from zinc oxide entities. The main stages of the present study includes the followings;

- Preparation of representative samples in order to use in characterization studies and laboratory tests.

- In order to investigate the mineralogical and chemical composition of the ore material, thermal behavior of the ore material,physical and chemical behavior of the ore, detailed characterization studies were conducted including; chemical analysis (ICP OES), Thermal analysis (TGA/DTA), mineralogical analysis as X-Ray diffraction (XRD) and mineralogical & petrographical analysis by using polished thin sections of the ore.
- In order to assess the particle distribution of the run of mine, particle size analysis were performed by using different sizes of sieves.
- Grindability tests were performed with the aim of providing sufficient degree of liberation for the subsequent flotation tests
- Flotation tests were conducted in order to determine optimum flotation parameters for the beneficiation of cerussite. Variable parameters are given in the below;
    - Reagent Dosage (sulfidizer dosage and collector dosage)
    - Conditioning Time
    - pH
- In order to determine the optimum leaching parameters and leaching reagents to achieve maximum extraction ratio for zinc, leaching test were conducted according to the two level full factorial statistical design (Box et al., 2005). In this context, design of experiments (DOE) was planned with respect to the two level full factorial statistical design. For the statistical design, effects of three parameters on leaching performance was investigated, as given below. Within the scope of the study, six different leaching reagents were used as sulphuric acid, ammonia, ammonium carbonate, ammonium chloride, boric acid and citric acid. According to the aforementioned different types of lixiviates, focused parameters during the leaching tests are as the followings;
    - Leaching time
    - Reagent Concentration
    - Leaching Temperature

3.2.1. Mineralogical-Petrographical Investigations and Assessment of Findings for Concentration Tests

Mineralogical and petrographical investigations were undertaken with the aim of protolith identification, ore and gangue mineralogy, and characterization of alteration/ mineralization styles. Mineralogical and petrographic analysis are performed by using three rock samples collected from Akdağmadeni area, Yozgat. Samples were cut into polished thin sections and petrographic studies were carried out using optical petrographic (Nikon brand polarized microscope) methods. All thin sections were photographed upon petrographic work.

3.2.1.1. Optical Microscope Analysis

According to optical microscope analysis it would be inferenced that, all samples have been intensely weathered and oxidized, and are characterized by predominant silica-clay-carbonate-oxide assemblages. As a result of intense weathering overprint, recognition of the original protolith was not possible neither at the hand specimen nor in thin section scale. Samples 2 and 3 present sub-rounded brecciated textures, whereas degree of brecciation is less significant for Sample 1. Moreover, all samples present at least minor vuggy to boxwork texture as a result of dissolution of soluble silicate and sulfide mineral species. Although intensely weathered, specimens are suspected to have undergone different degrees of quartz-sericite alteration and possible hydrothermal silicification prior to near-surface weathering and oxidation. All samples contain cerussite and smithsonite which was likely formed due to weathering of their sulfide counterparts. With the consideration of cerussite contents of samples are as follows Sample 1> Sample 2> Sample 3. Remnant galena was not found in any of the samples, however ghost galena grains were tentatively defined in Sample 1. Pyrite is the single sulfide mineral presented in the all samples and has been oxidized initially into hematite and later into goethite and lesser limonite during near-surface supergene weathering.

Based on the mineralogical and petrographical analysis of Sample 1 which is presented in the Figure 3.1, sample shows a highly weathered and silicified/ oxidized rock, which generally appears as massive to slightly brecciated. As it can be seen in the Figure 3.1 rock is predominantly light brown and locally white to light green in color. White areas refer to quartz and prismatic lead carbonate minerals while green coloring is suspected to be due to occurrence of smithsonite and other silicified zinc species. Few tiny specks of a metallic gray mineral (possibly galena) were also identified. These are inconspicuously surrounded by white to translucent, elongated to stubby prismatic crystals of cerussite. Dendritic manganese oxide coatings were developed on fracture surfaces. Sample showed weak but consistent reaction to dilute HCl, suggesting abundant presence of carbonate minerals (cerussite and smithsonite).

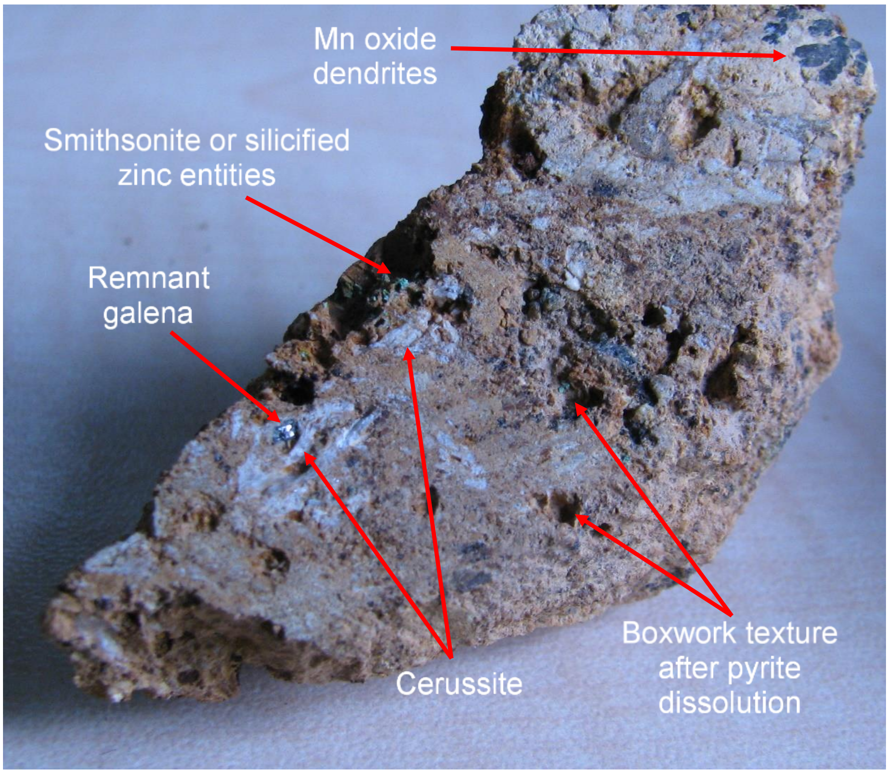


Figure 3.1 Macrophotograph of Sample 1

Under microscope, the sample is characterized by an assemblage of quartz, clay /sericite, oxide, carbonate and sparse sulfide (pyrite) mineral phases replacing the original protolith. This protolith was initially subjected to hydrothermal alteration, which resulted in formation of fine-grained quartz and sericite (either muscovite or illite), and was later undergone intense weathering. The predominant mineral in the sample is quartz, which occurs either as very fine-grained masses or as elongated prismatic crystals. Based on the conducted analysis, quartz-sericite assemblage is paragenetically the earliest mineral association identified with in the sample while, most of the sericite has been transformed to clay minerals namely kaolinite due to intense weathering and supergene oxidation (Figure 3.2 - 3.4). Although rare crystals of a metallic gray cubic mineral resembling galena (Fig. 3.1) were observed in hand specimen, this mineral was not identified confidently under microscope. Rather, all of galena – if originally present – has most likely been completely replaced by cerussite (Figs. 3.3 and 3.6). In the case of reflected light exposure to the hand specimen, it was determined that sample contains minute dissemination of remnant (pre-oxidation) pyrite (Figure 3.7) which was likely intergrown with fine-grained quartz and sericite. Much of the pyrite has been readily oxidized into hematite or goethite/limonite (Figure 3.7 and 3.8). Hematite usually pseudomorphs pyrite as it is present in the sample in cubic or pyritohedron forms, whereas goethite and/or limonite generally occurs along microfractures or as concentric layers (Figure 3.7 and 3.8).

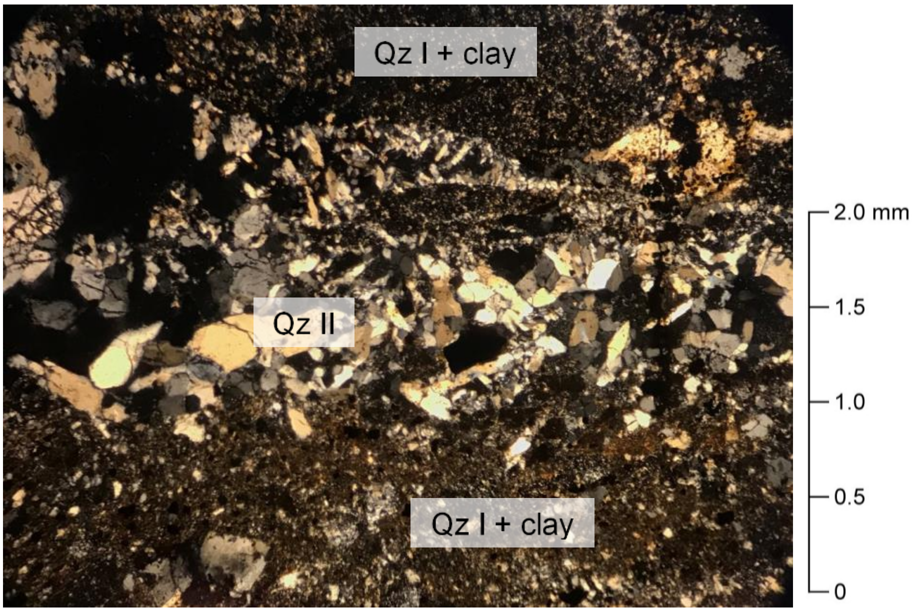


Figure 3.2 Filling Coarse-Grained Quartz

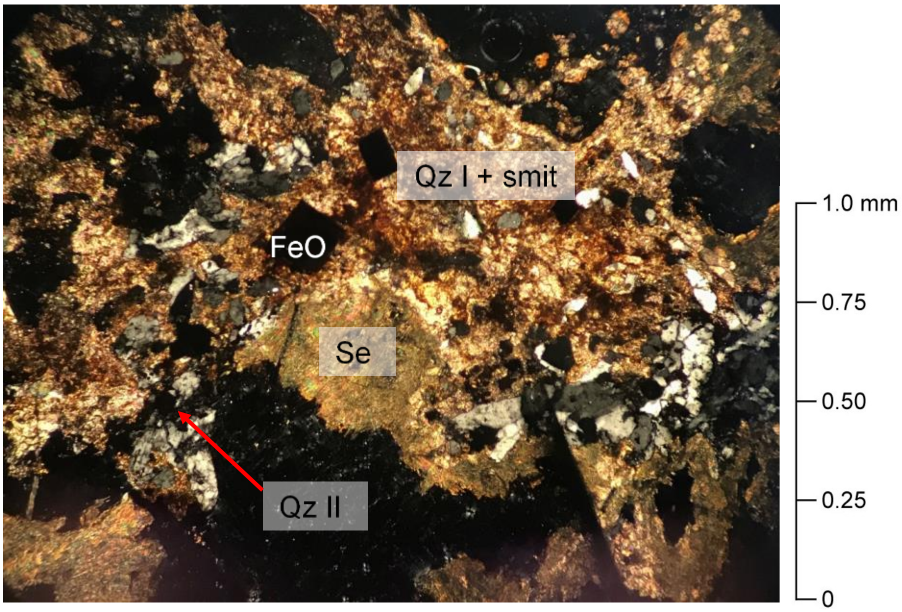


Figure 3.3 Intergrowths of early fine-grained quartz (Qz I + smithsonite), euhedral Fe-oxide (pseudomorphing early pyrite) and remnant sericite (Ser) that has now been largely replaced by clay minerals. Coarse-grained quartz (Qz II) cross-cuts earlier mineral phases (transmitted cross-polarized light)

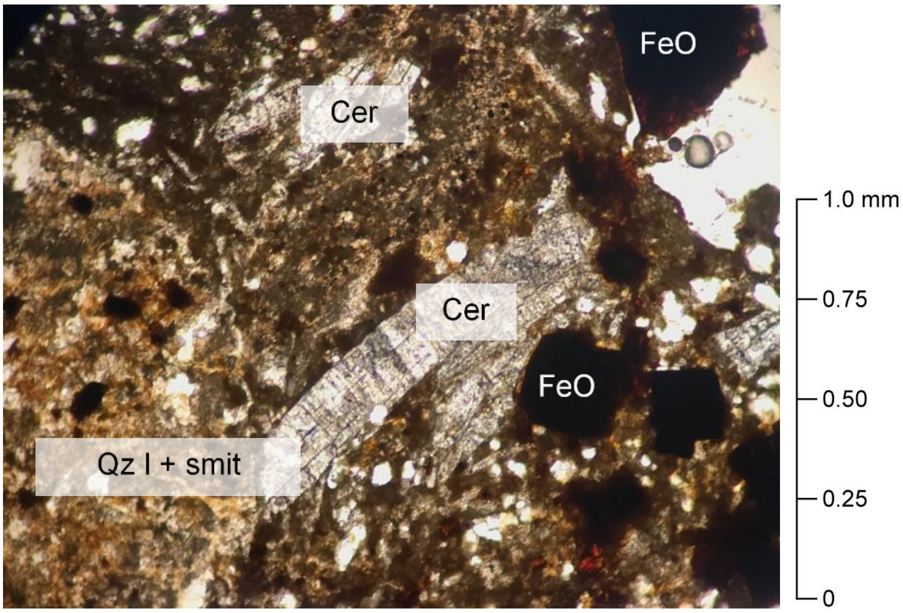


Figure 3.4 Elongated prismatic cerussite (Cer) grains surrounded by fine-grained quartz, smithsonite, clay, and Fe-oxide (after pyrite) assemblage (transmitted plane polarized light).

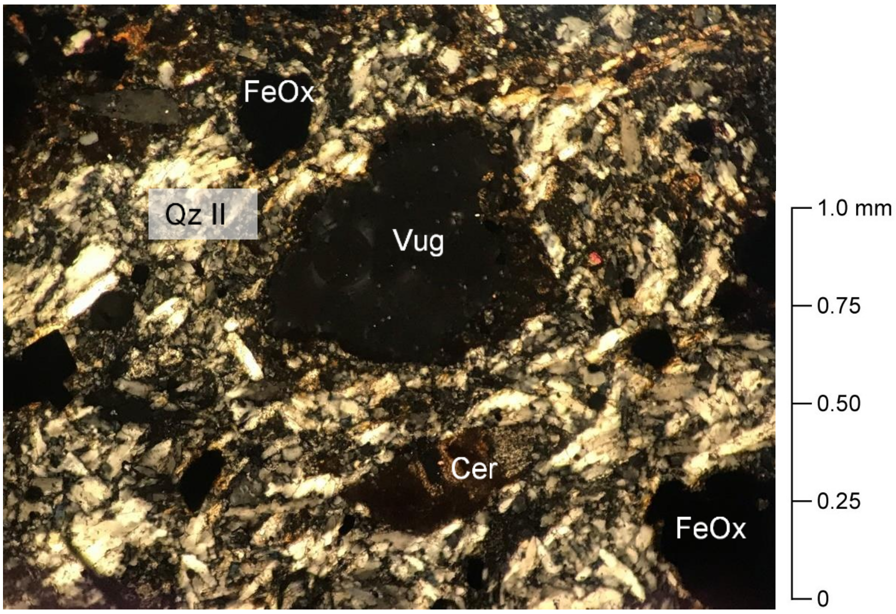


Figure 3.5 Deformed grains of late coarse-grained prismatic quartz (Qz II) intergrown with cerussite (Cer) and Fe-oxide (after pyrite), surrounding the central vuggy cavity (transmitted cross-polarized light).

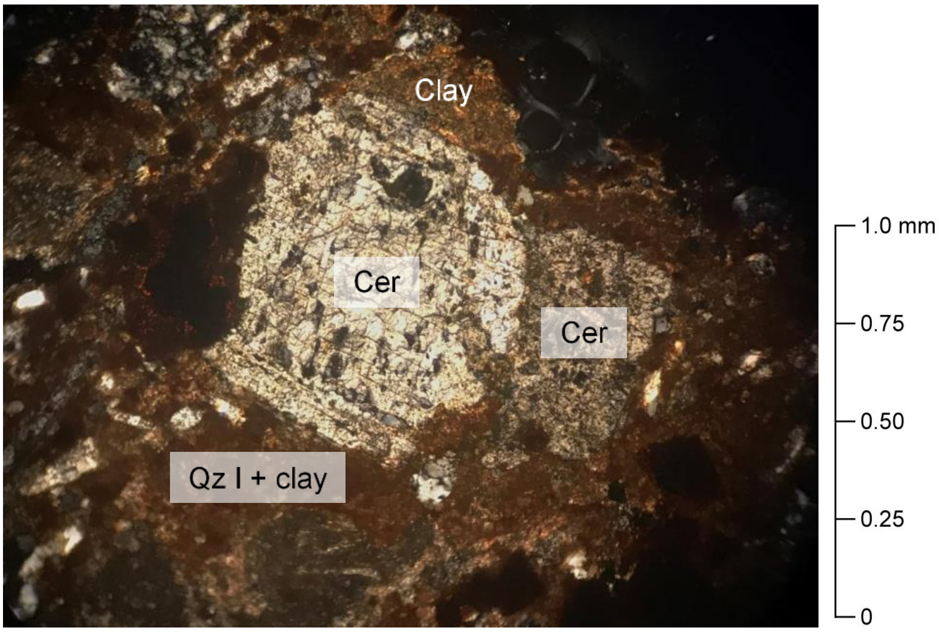


Figure 3.6 Large equant cerussite (Cer) grain (after galena) surrounded by fine-grained quartz (Qz I) and clay (transmitted cross-polarized light).

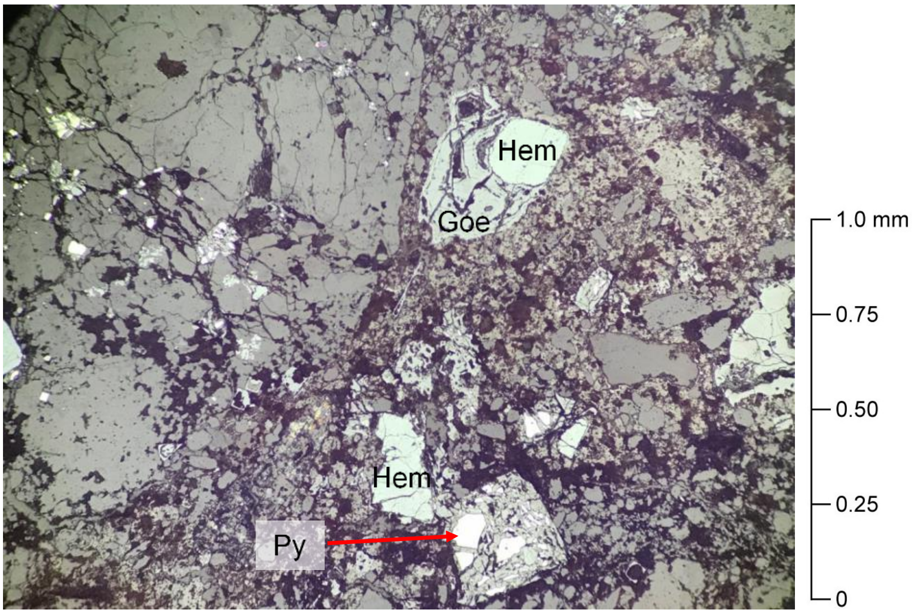


Figure 3.7 Remnant pyrite (Py) replaced by pseudomorphous hematite (Hem) and concentric layers of goethite (Goe; reflected plane-polarized light).

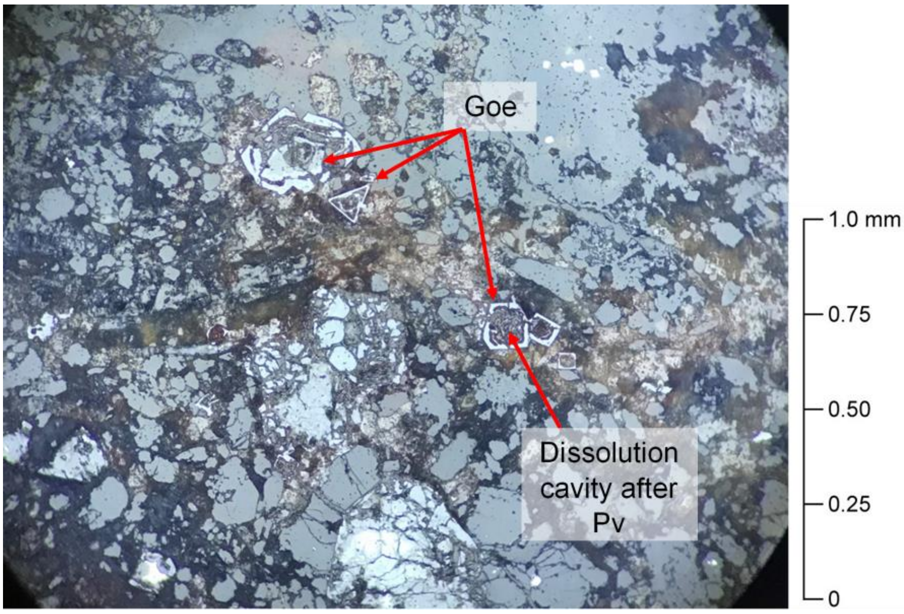


Figure 3.8 Goethite (Goe) formation after dissolution and leaching of early euhedral pyrite (reflected plane-polarized light).

Based on the mineralogical and petrographical analysis of Sample 2 which is presented in the Figure 3.9, sample shows a highly weathered and silicified/ oxidized rock. In addition to that, two discrete layers are visible in hand specimen; one with tan to beige in color and consists of silica, clays and carbonates (possibly cerussite and smithsonite), and a darker orange colored layer with boxwork textures partly filled by goethite or limonite. In the cut surface, stubby prismatic crystals of cerussite are visible around dissolution cavities formed after leaching of earlier soluble minerals. Sample reacted weakly with dilute HCl, suggesting presence of carbonate minerals (cerussite and smithsonite).

Figure 3.9 Macrophotograph of Sample 2

In this context it was determined that the sample displays brecciated texture and has been intensely weathered into a clay-silica-carbonate assemblage. The breccia has a heterolithic character and it is composed of subrounded to rounded clasts. Some of these clasts clearly display remnant igneous texture (Figure 3.10), whereas others consist of quartz-carbonate or quartz-carbonate-clay assemblages with unknown origin. Quartz is the most abundant mineral in the sample and occurs in several different varieties. Very fine grained quartz is accompanied by sericite (or later clay), and these either occur within breccia clasts of igneous origin (Figure 3.10) or within the breccia matrix. Most of the sericite in the igneous breccia clasts or in the breccia matrix, however, have been transformed to clay minerals namely kaolinite during weathering and supergene oxidation. Another variety of coarse-grained (>100 μm) quartz was identified as prismatic elongated crystals, and these occur within breccia clasts together with medium- to coarse-grained (up to 1 mm in length) cerussite (Figure 3.11). These quartz-cerussite-bearing clasts have been slightly deformed as indicated by sheared grains (Figure 3.11). Large triangular pits observed within cerussite grains (Figure 3.12) suggests formation after galena most likely due to weathering and oxidation. On the other hand, no galena was observed under microscope. Under reflected light, the only observed sulfide mineral was pyrite to a lesser extent, which forms disseminations of euhedral grains (Fig. 13). However, much of this mineral was oxidized into Fe-(hydr)oxide phases such as hematite and goethite. Hematite pseudomorphs occur as euhedral grains after pyrite (Fig. 14), whereas goethite was observed commonly as a fracture fill material after leaching of secondary hematite under oxidizing and hydrous weathering conditions.

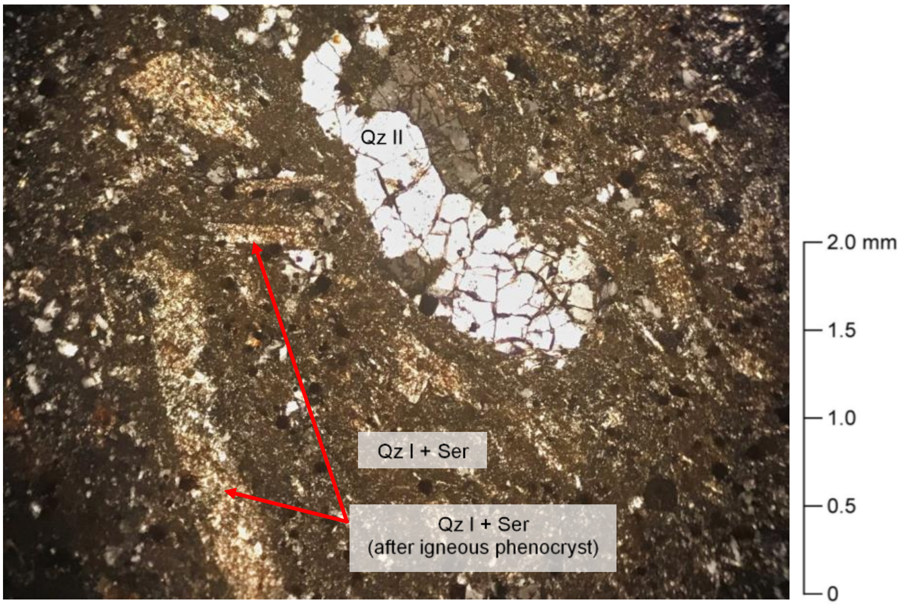


Figure 3.10 Igneous rock clast altered into fine-grained quartz (Qz I), sericite (Ser), and pyrite (opaque grains). Elongated prismatic grains visible to the left side of the image were initially igneous ferromagnesian minerals replaced by quartz and sericite. Coarse-grained quartz (Qz II) overprints this early assemblage (transmitted cross-polarized light)

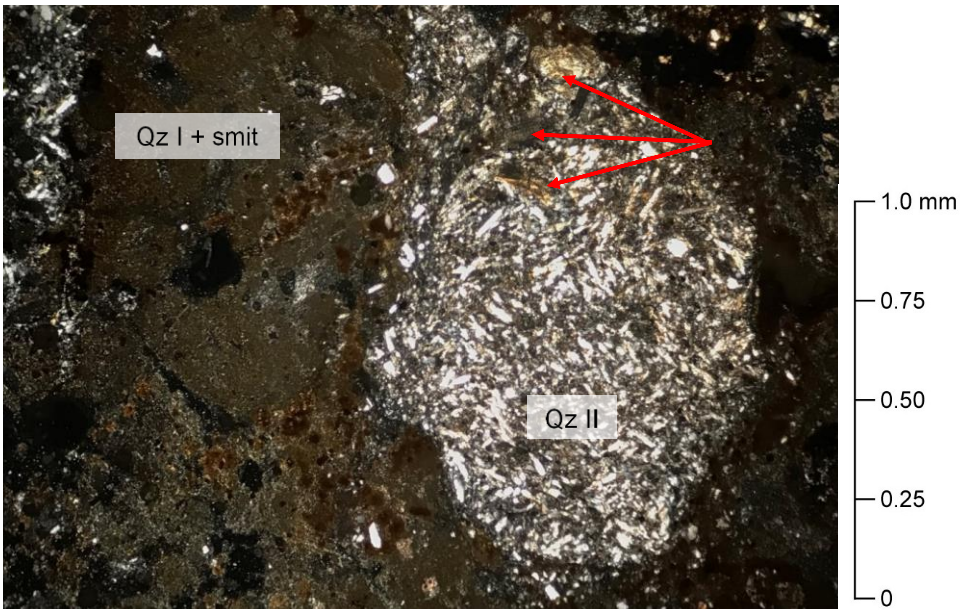


Figure 3.11 Breccia clast consisting of coarse-grained prismatic quartz (Qz II) and cerussite (Cer) surrounded by fine-grained quartz (Qz I) and smithsonite

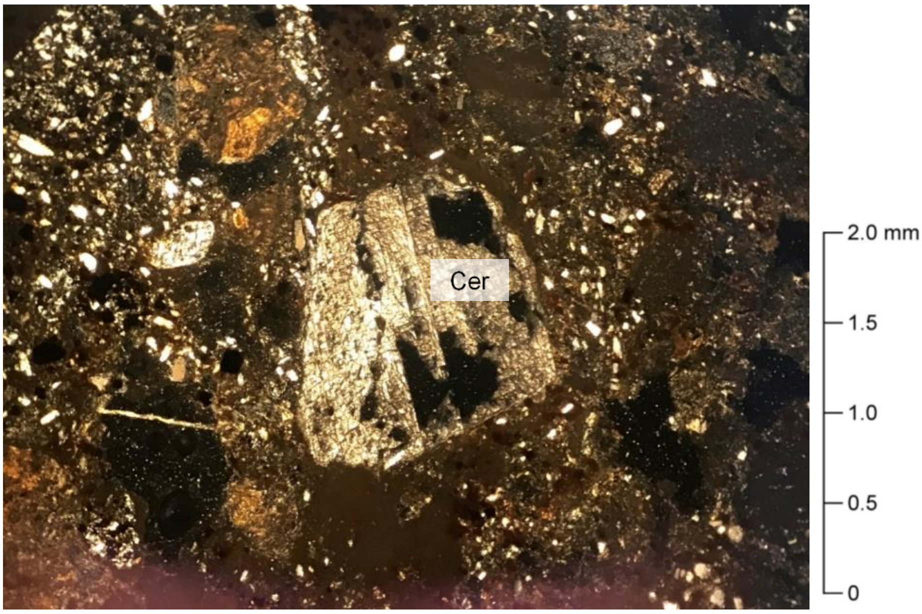


Figure 3.12 Cerussite (Cer) grain consisting of triangular pits (black) indicating formation after galena (transmitted cross-polarized light).

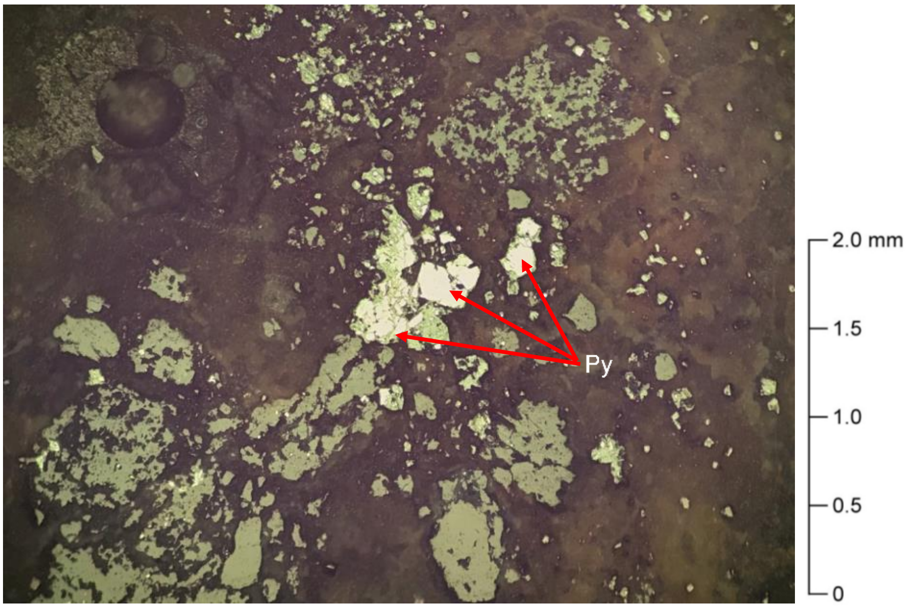


Figure 3.13 Remnant euhedral pyrite (Py) grains (reflected plane-polarized light).

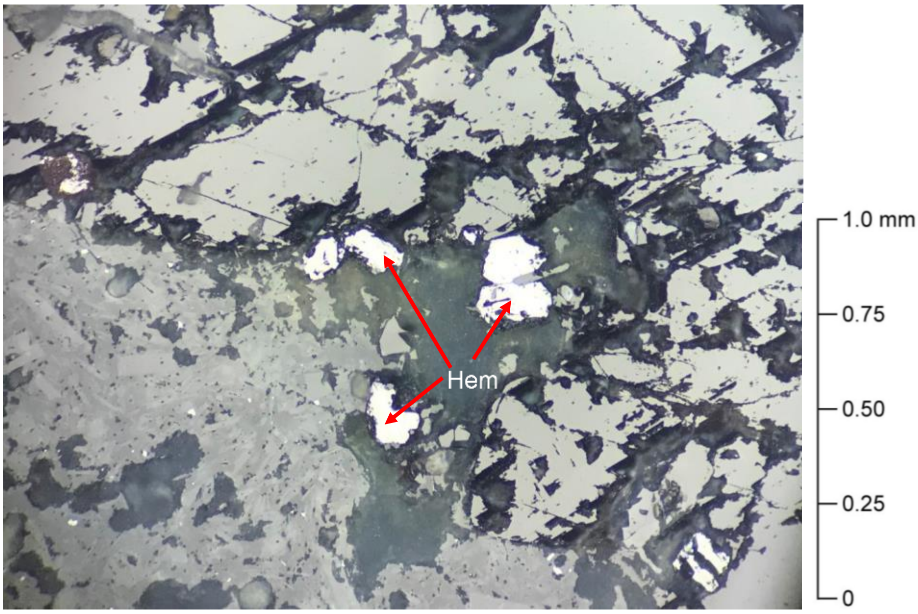


Figure 3.14 Hematite (Hem) grains formed after oxidation of early pyrite (reflected plane-polarized light)

Based on the mineralogical and petrographical analysis of Sample 3 which is presented in the Figure 3.15, the outcrop sample represents a strongly weathered and silicified/oxidized rock, which generally appears as massive with minor cavities. Rock is predominantly light brown and locally white to light green in color. White areas consist of quartz, clay, and carbonate minerals, whereas green coloring area represents to smithsonite. Sample react very weakly with dilute HCl, suggesting presence of minor amounts of carbonate minerals (cerussite and smithsonite). However, attraction to magnet was not detected.

Figure 3.15 Macrophotograph of off-cut slab of Sample 3

According to mineralogical and petrographical observations it was determined that the sample is intensively weathered into an assemblage of silica-clay-carbonate, rendering the origin of the protolith impossible. In addition, the amount of carbonate in this sample is significantly lower than that of other studied samples, while the amount of silica is consequently much higher. Under microscope, two separate clast types were identified; one with fine-grained texture and characterized by complete replacement by silica and clay, and another one consisting of coarse-grained crystals of prismatic quartz. Clay observed in clasts and as matrix material is likely the weathering product of earlier sericite, but unlike Samples 1 and 2, Sample 3 does not contain any sericite. This likely indicates that the degree of weathering is notably stronger in this sample than others. Individual grains of sparse cerussite, which probably formed as a weathering product of galena, was identified in the sample (Figure 3.16 and 17). However, its overall abundance is much lower compared to Samples 1 and 2. Under reflected light, pyrite occurs as remnant grains (Figure 3.18) and most of this mineral has been oxidized into hematite (showing pyritohedron form; (Figure 3.19). Concentric layers or fracture filling goethite formed after further oxidation (Figure 3.19) and leaching of both pyrite and hematite under near surface oxidizing conditions.

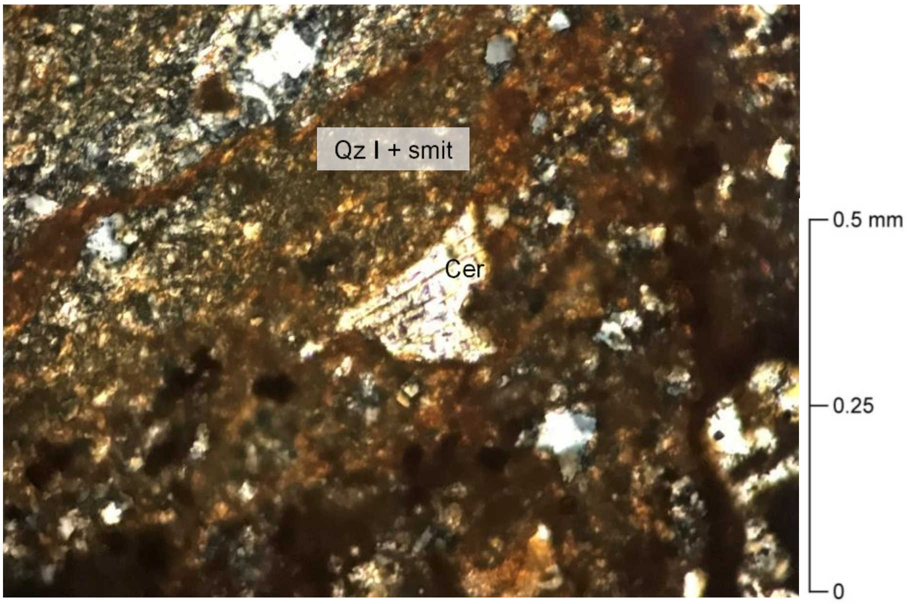


Figure 3.16 Isolated cerussite (Cer) grain surrounded by fine-grained quartz and smithsonite (Qz I + smit) and clay. Opaque grains are hematite or goethite and goethite-filled brown veinlets cross-cut through the sample (transmitted cross-polarized light).

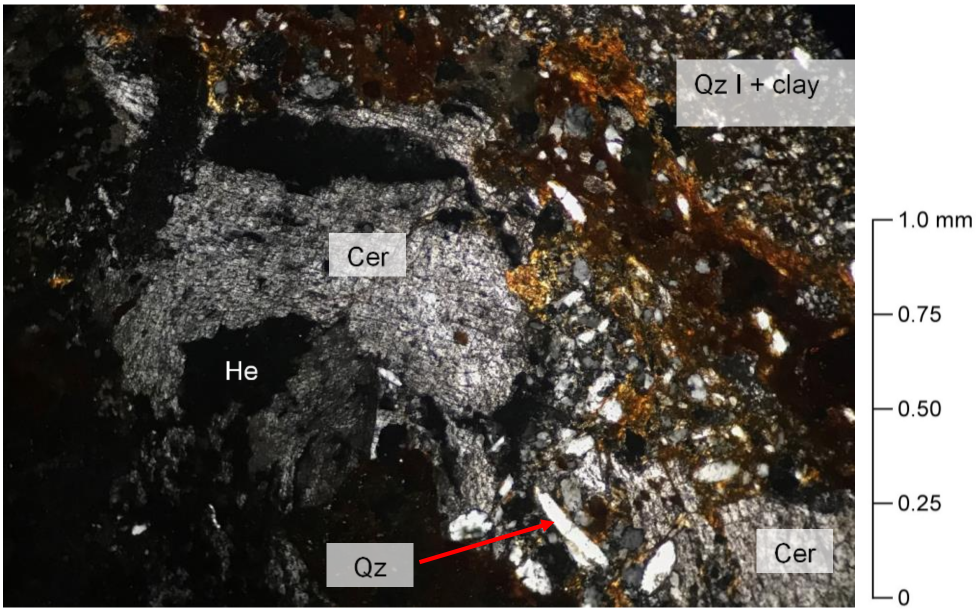


Figure 3.17 Large cerussite (Cer) grains developed near a cavity. Immediate surrounding area consists of hematite (Hem) and coarse-grained quartz (Qz II), whereas area to the top right consists of fine-grained quartz (Qz I) and clays. Brown coloring is due to fracture-filling goethite (transmitted cross-polarized light).

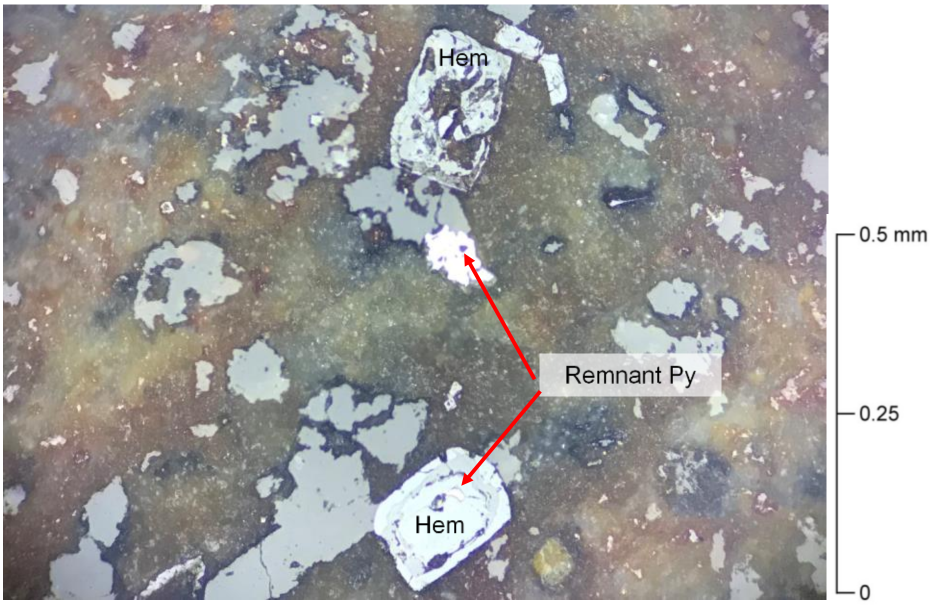


Figure 3.18 Euhedral pyrite (Py) grains almost completely replaced by hematite (Hem; reflected plane-polarized light).

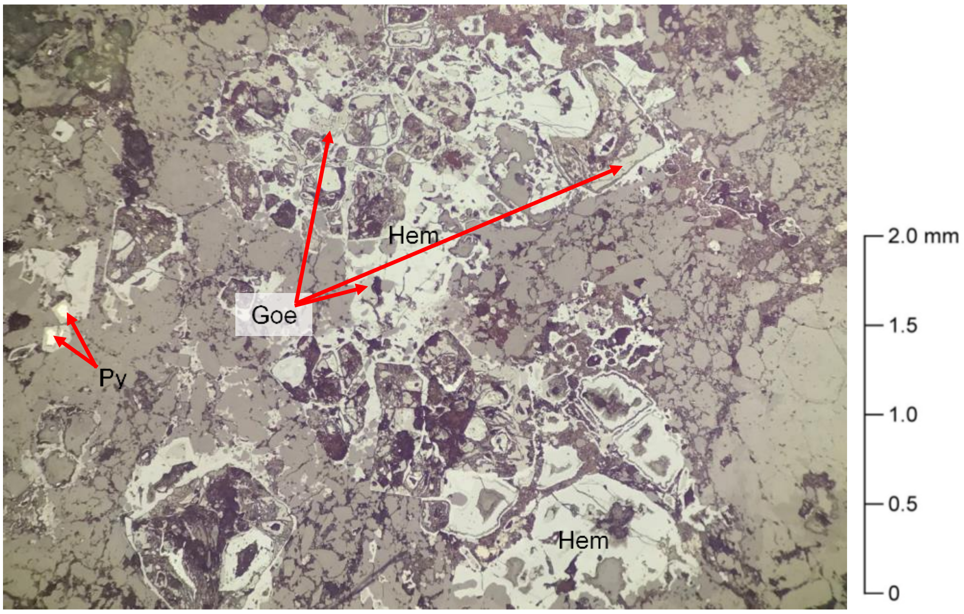
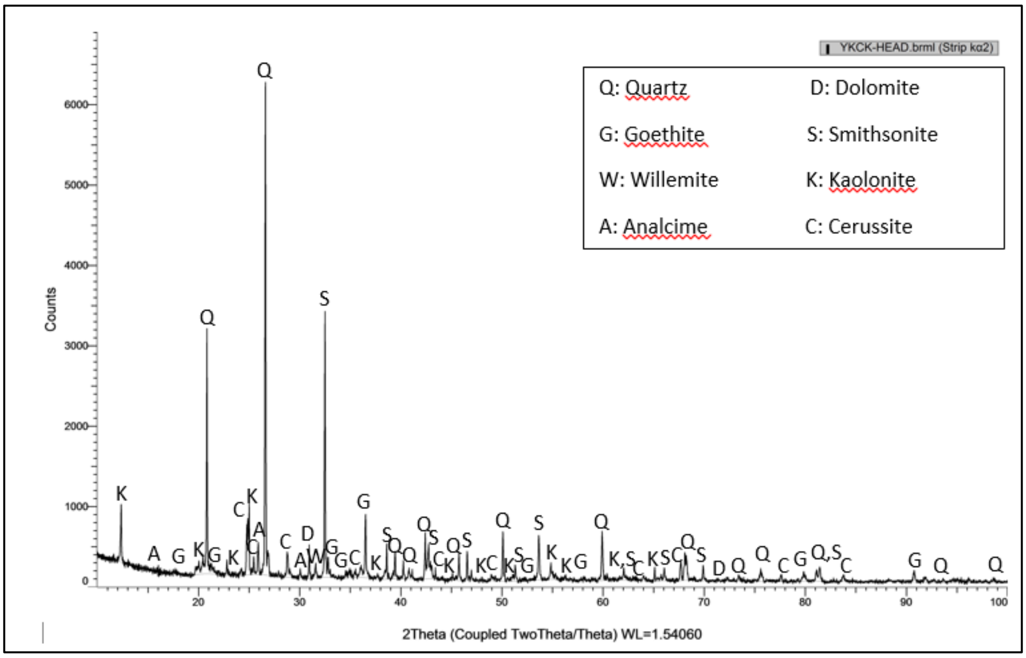


Figure 3.19 Pyrite (Py) grains completely replaced by hematite (Hem) and goethite (Goe; reflected plane-polarized light).

3.2.1.2. XRD Analysis

In order to investigate the mineralization occurred in the Yozgat - Akdagmadeni carbonaceous lead-zinc ore, XRD analysis was conducted. The main objective of mineralogical, XRD analysis is prove of minerals specified with the help of optical microscope analysis. XRD analysis of the head sample indicated that, Yozgat carbonaceous lead-zinc ore mainly consists of quartz, smithsonite, kaolinite, cerussite, willemite, goethite, dolomite and to a lesser extent analcime. X-ray diffractogram of the head sample is given in Figure 3.20.

According to the performed mineralogical, XRD analysis, Quartz is the major mineral phase within the ore sample and presented by the most intense peak at 26.62° and 20.84°. Moreover, less intense characteristics peaks of quartz are presented at 36.52°, 39.45°, 42.43°, 45.76°, 50.10°, 59.92°, 68.10° and 68.28°. Moreover, as a carbonate mineral, characteristic peak of dolomite was observed at 31.02°. In addition, as another gangue mineral contained in the ore kaolinite is observed at 26.62°, 28.83°, 12.36°, 20.46°, 32.82°, 38.63°, 42.43°, 42.86°, 50.24°, 53.65°, 59.62°, 60.06°, 68.20°, 68.28° and 81.42°. As the valuable part of the ore, main characteristic peaks of smithsonite were seen at 32.51°, 25.01°, 38.72°, 42.86°, 53.76°, 68.28° and 81.42°. Also, characteristic peaks of lead carbonate, namely cerussite were seen at 25.47°, 30.95°, 42.75°, 45.76°, 59.92°, 60.06°, 67.72° and 81.42°.



3.2.2. Thermal Characterization of the Ore

Thermal characterization of the ore sample was performed by using Thermogravimetric/ Differential Thermogravimetric (TG/ DTG) and Differential Scanning Calorimetry (DSC) analysis. Based on the carbonaceous structure of the ore material, thermal characterization of the ore is important since carbonate entities decomposes at high temperatures by releasing carbon dioxide. In this context, TG/ DTG determines the weight loss of the ore sample according to the changes in temperature. In addition, DSC provides knowledge about whether the ore presents endothermic and/or exothermic behavior with respect to energy change defined as heat flow. Thermal characterization of the ore was determined by using Perkin Elmer Simultaneous Thermal Analyzer (STA 6000). TG/ DTG and DSC were conducted both in pyrolysis (inert) and combustion environment. During pyrolysis N_2 was used as inert gas, while during the combustion analysis O_2 was used . Analysis were carried out between 30 ° C and 900°C with 10°C/min increase in temperature and 20ml/min gas flow was provided. Thermal behavior of the ore would be seen in following figures which were derived from thermal characterization tests. The obtained results from both pyrolysis and combustion analysis of the ore sample provide coherent information. Based on the results of thermal analysis, namely TGA and DTG profile of the ore sample, it was determined that there was four main reaction areas as 50 to 200 °C, 250 to 350 °C, 350 to 450 °C and 550 to 800°C. Within the consideration of TGA/ DTG profiles of the ore sample it would be seen that the weight loss starts at very low temperature as approximately 50 °C and continues until 200 °C due to the loss of moisture content and inherent moisture content. Apart from that, there was seen a relatively sharp weight loss between 250 and 350 °C mostly because of the decomposition of the CO_2 content of the zinc carbonate, namely smithsonite (Alhawi, Rehan, York, & Lai, 2015). In the context of the third reaction, namely from 350 to 450 °C, hydroxide content of clay minerals and also the iron containing goethite entities were lost. Based on the fourth reaction zone above approximately 600 °C decomposition of carbonate containing gangue entities such as dolomite was decomposed by releasing their carbon dioxide content As the result of the thermal analysis, it was seen that approximately %10 by weight of the material was lost due to occurred reactions.

Figure 3.20 TGA/ DTGA Profile of the Ore by Using Combustion Method

Figure 3.21 TGA/ DTGA Profile of the Ore by Using Pyrolysis Method

The DSC profiles of the ore sample are given in the Figure 3.23 and Figure 3.24. Based on the performed pyrolysis and combustion analysis, it was seen that the endothermic reaction occurs between 550 to 600 °C was mainly due to the decomposition of carbonate containing gangue entities, as dolomite including calcite. Apart from that, observed endothermic peak between approximately 700 °C might be occurred due to the decomposition of the dolomite without containing calcite.

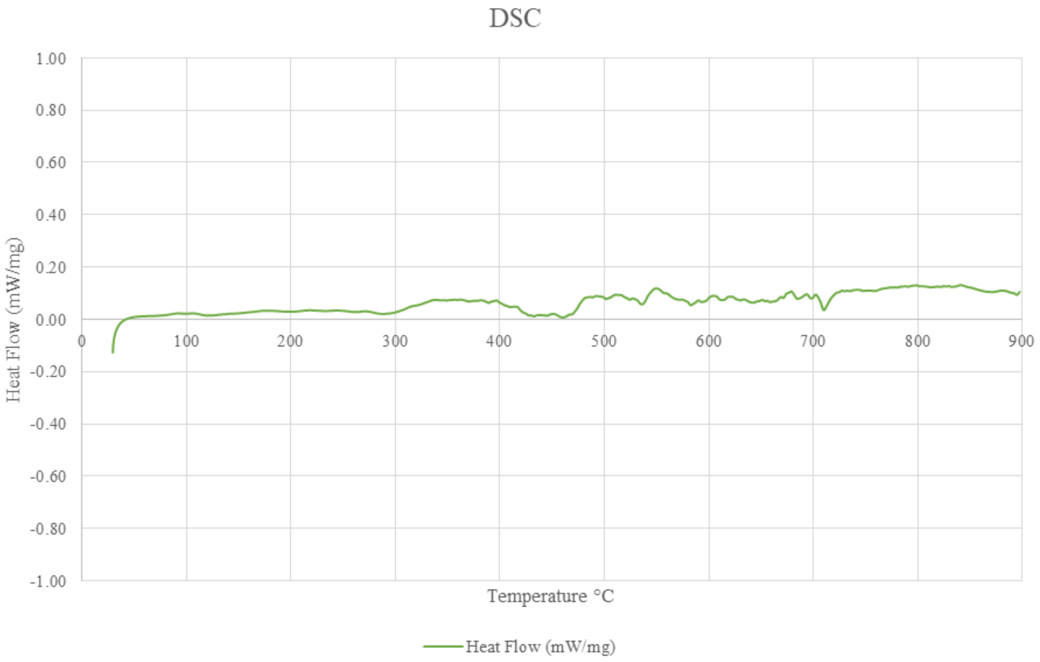


Figure 3.22 DSC Profile of the Ore by Using Combustion

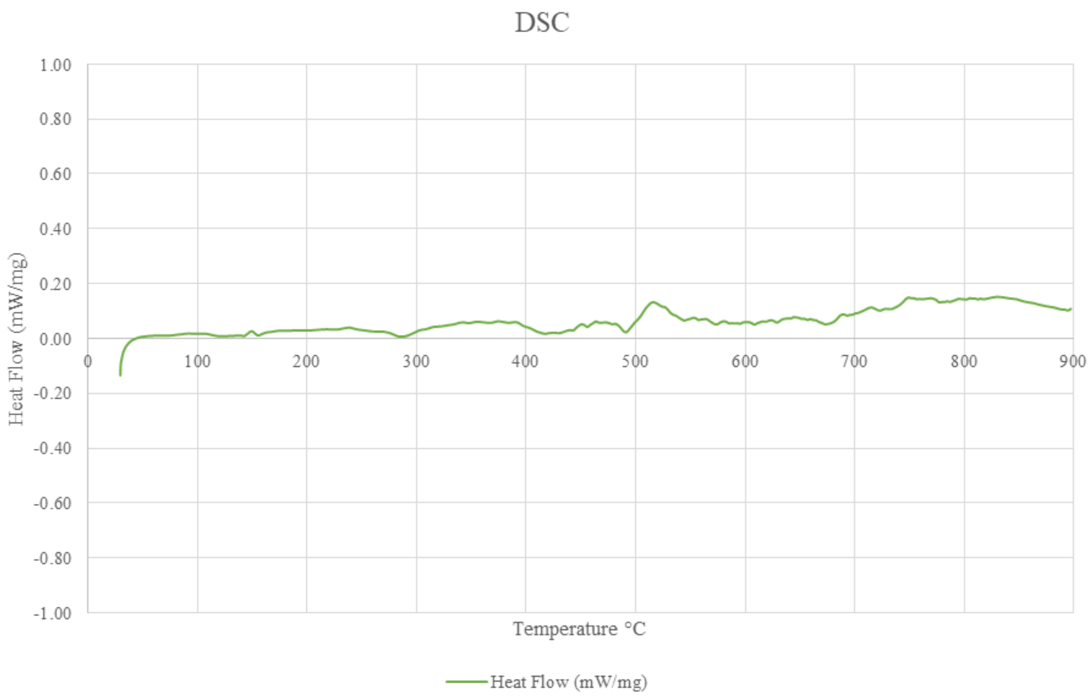


Figure 3.23 Figure 17 DSC Profile of the Ore by Using Pyrolysis Method

3.2.3. Preparation of Representative Ore Samples

Representative sample preparation was performed in order to use in characterization and concentration tests. Prior to the preparation of representative samples, in order to determine moisture content of the run of mine ore, moisture content analysis was conducted. For these tests approximately 50 grams of representative samples were used and 6 parallel tests were conducted. Basically, each representative samples were placed into the container and weighed. After that, container was placed into the laboratory type furnace which is operated at nearly 105 ± 5°C. During the tests, periodic measurements were done and after samples reached constant weight, they were taken out from the furnace. By using the records taken from measurements and by using the following formulas moisture content of the ore is determined.

$$w = [\,(M_{cms} - M_{cds}) / (M_{cds} - M_c)] \times 100 = (M_w / M_s) \times 100$$

w = moisture content, %

M_{cms} = mass of container + moist sample

M_{cds} = mass of container + dry sample

M_c = mass of container

M_w= mass of water ($M_w = M_{cms} – M_{cds}$)

M_s = mass of oven dry sample ($M_s= M_{cds} = M_{cds} – M_c$)

As the result of the moisture content analysis, average moisture within the run of mine ore is calculated as 10.61% by weight. Constructed weight percentage – time graphs for determining the moisture content of samples is given in Figure 3.25.

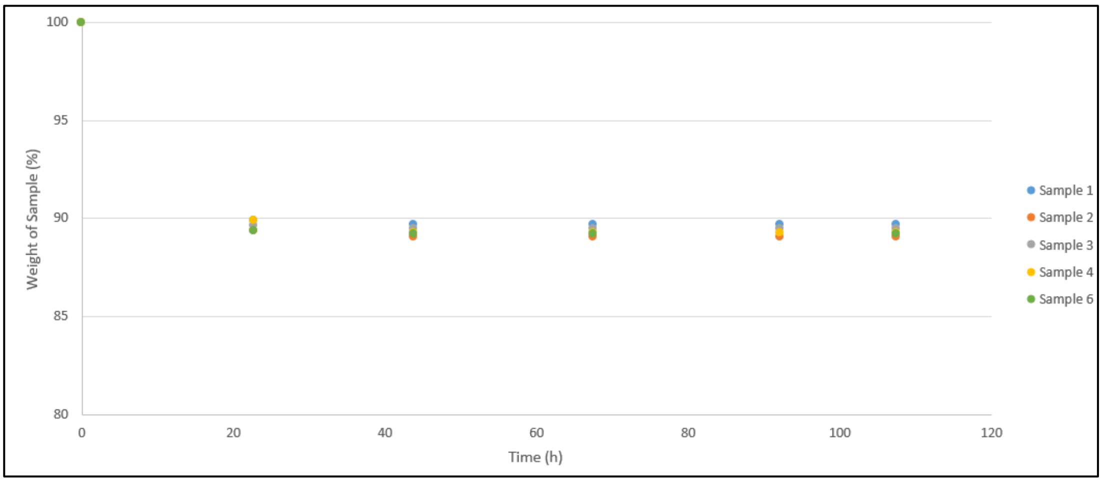


Figure 3.24 Graph for the Determination of the Moisture Content

Following the moisture content analysis of r.o.m., representative samples were prepared for the both characterization and concentration studies. Representative samples were prepared by using cone and quartering method and Jones Riffle separators in various sizes. At the end of this procedure, representative samples weighing approximately 400 gr were obtained in order to use in the flotation concentration studies. Part of the representative samples were taken in order to use in characterization studies. Flow sheet that belongs to the preparation of the representative samples is given in the Figure 3.26.

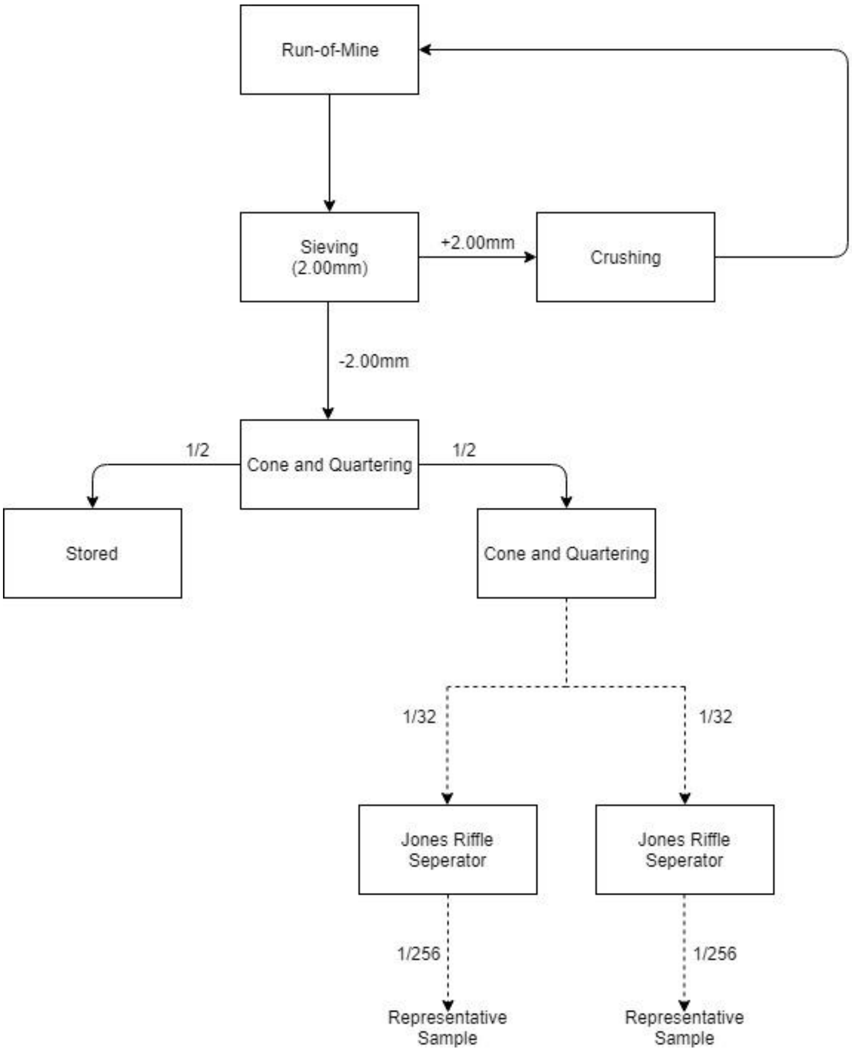


Figure 3.25 Representative Sampling Flowsheet

As it can be understood from the representative sampling flowsheet, dry sieving was made to run of mine by using 2.00 mm sieve. Oversize material with particle size greater than 2.00 mm was crushed by using both jaw and roll crushers. Following this, material with particle size less than 2.00 mm was mixed in accordance with the standard sampling method as coning and quartering. Cone and quartering method was conducted until each representative samples weight as approximately 6.25 kg. Then, the samples were separated by using Jones Riffle separator and each representative sample weight was reduced to nearly 400 gr. Figure 3.27 presents the run of mine, crushed ore with particle size -2.00m, representative sampling by using cone and quartering method and representative sampling by using Jones Riffle.

Figure 3.26 Representative Sample Preparation Procedure: a) Run of Mine Ore b) Crushed Ore Sample c) representative sampling by using cone and quartering method d) representative sampling by using Jones Riffle.

3.2.4. Chemical Analysis of Representative Sample

In order to examine the chemical composition of the r.o.m., elemental analysis were conducted using previously prepared representative samples by the ICP-OES method and general elemental composition of the ore was determined. The elemental analysis result of the representative ore sample is given in the Table 9.

Table 3.1 Elemental Analysis of Representative Sample

Sample Code	Pb (%)	Zn (%)	Fe (%)	Al (%)	Ca (%)	Mg (%)	Si (%)
Head	3.17	6.19	6.72	4.35	0.61	0.52	23.2

Chemical analysis of the head sample presents that elemental content of lead in the ore is 3.17%. With the consideration of X-Ray Diffractometer analysis results, whole lead content refers to the cerussite. In addition to that, according to elemental analysis of the head sample zinc content of the ore was determined as 6.19% which would be contained within the structure of smithsonite and willemite which is also consistent with the conducted mineralogical analysis indicating that most of the zinc content is generated due to the presence of smithsonite while remaining part would be originated from willemite due to the presence of peaks with low intensity belongs to willemite.

In terms of impurity content of the ore sample, Fe and Si would be thought as the major impurities with the content 6.72% and 23.2% respectively. Within the consideration of mineralogical characterization studies elemental content of iron might be originated from goethite and clay entities. As the most dominant gangue entity, presence of Si is pretty higher as it was expected since quartz (SiO_2) has responsible for the most intense peaks of X-Ray diffractogram. Beside from the quartz, Si content would be originated from kaolinite ($Al_2Si_2O_5(OH)_4$), analcime ($NaAlSi_2O$) and willemite (Zn_2SiO_4). Moreover, except from silica minerals, high silica content would be resulted from the clay minerals. Relatively higher content of the Al having the percentage of 4.35% would be resulted from the presence of kaolinite since it would be accepted as one of the gangue mineral determined in X-Ray diffractogram. Moreover, presence of Ca and Mg proves the presence of carbonaceous minerals.

3.2.5. Specific Gravity Determination

In order to perform a more detailed physical characterization, specific gravity of Yozgat - Akdağmadeni ore sample was determined by using pycnometer. Prepared representative samples were used within the context of specific gravity determination studies. Two parallel tests were conducted in order to obtain more coherent results. The main objective of the specific gravity determination studies is to examine the possibility to apply gravity separation within the consideration of pre-concentration methods. Calculation of the specific gravity is performed according to following formula;

$$\text{Specific Gravity} = \frac{(P2-P1)}{[(P2+P4)-(P1-P3)]}$$

P_1 = Weight of pycnometer

P_2= Weight of pycnometer + Weight of Sample

P_3 = Weight of pycnometer + Weight of Sample + Weight of Distilled Water

P_4 = Weight of pycnometer + Weight of Distilled Water

Experimental parameters of the specific gravity determination test is given in the Table 3.2.

Table 3.2 Specific Gravity Determination of the Representative Samples

Sample Code	**P_1**	**P_2**	**P_3**	**P_4**	**Specific Gravity**
Head - 1	28.61	31.53	80.44	78.51	2.95
Head - 2	28.55	31.71	80.58	78.49	2.95

As the result of specific gravity determination work, specific gravity of the r.o.m. ore samples were calculated as 2.95. Since the specific gravity of the representative ore sample is relatively low, application of gravity concentration method as a pre-concentration method seems to be challenging. In addition to that, relatively lower specific gravity value confirms contamination of the valuable content of the ore by clay and carbonaceous minerals.

3.2.6. Sieve Analysis

In order to gain information about the particle size distribution and the corresponding elemental distribution of the ore sample wet sieve analysis was performed. According to wet sieve analysis, lead and zinc content with respect to particle size distribution was examined. Moreover, in order to evaluate potential effect of desliming before flotation, particle size distribution of impurities was considered. Approximately 800 gr representative (crushed down to -2.0mm) sample was used to conduct wet sieve analysis. Representative sample was steeped prior to sieve analysis in order to prevent mineral surface coating of clay minerals and to support dispersion of clay minerals. Particle size distribution of -2 mm Yozgat, Akdagmadeni ore is given in the Table 3.3 and Figure 3.28.

Table 3.3 Particle Size Distribution of the Representative Ore Sample

Fraction	**Total Weight (g)**	**Percentage Weight**	**Cum Over Size (%)**	**Cum Undersize (%)**
+1.2mm	147.16	19.89	19.89	80.11
-1200+850µm	138.50	18.72	38.61	61.39
-850+500µm	113.73	15.37	53.98	46.02
-500+300µm	104.30	14.10	68.08	31.92
-300+150µm	49.43	6.68	74.76	25.24
-150+106µm	26.76	3.62	78.37	21.63
-106+75µm	23.29	3.15	81.52	18.48
-75+53µm	17.66	2.39	83.91	16.09
-53+38µm	11.10	1.50	85.41	14.59
-38+20µm	14.85	2.01	87.41	12.59
-20µm	93.13	12.59		
Total	**739.91**	**100.00**		

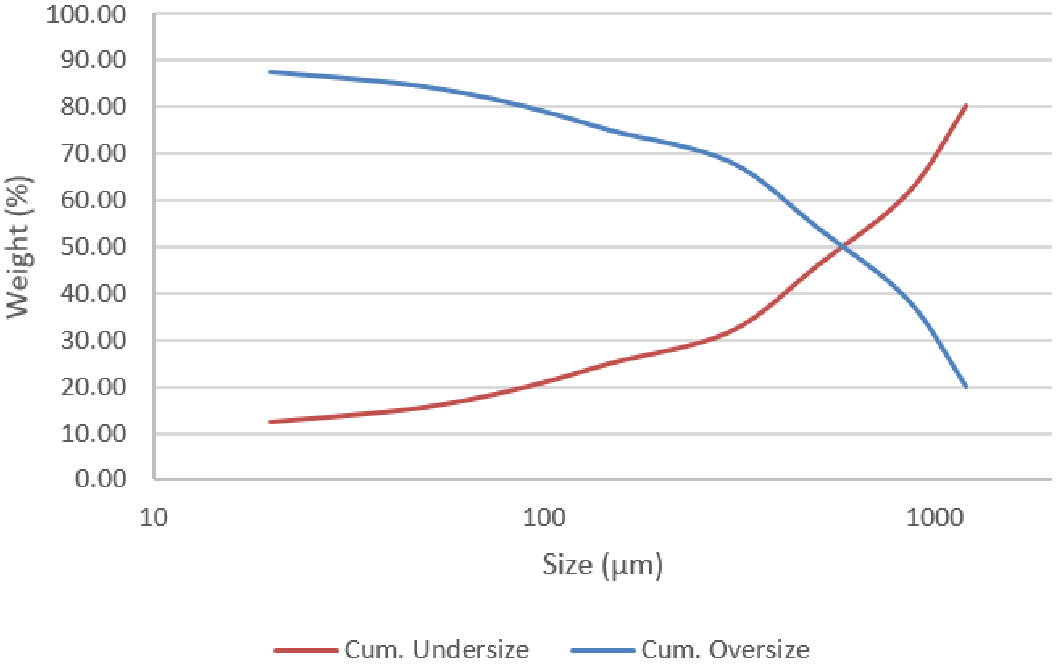


Figure 3.27 Particle Size Distribution of the Representative Sample

According to obtained particle size distribution graph seen in Figure 3.28, d_{80} and d_{50} of the ore was determined as 1198.49 µm and 573.670 µm respectively.

Elemental analysis of each particle size fraction is conducted by using ICP-OES method. Based on the elemental analysis results, metallurgical balance table for the lead and zinc and also the impurities was obtained for obtaining information about the distribution of elements with respect to the particle size. Metallurgical balance table is given in the Table 3.4. Within the consideration of desliming before the flotation, it would be beneficial to evaluate particle size distribution and corresponding elemental analysis. As it can be seen in Table 12, 9.53% of lead content have the particle size smaller than 20 µm with 2.33% of Pb grade and 10.23% of zinc contents have the particle size smaller than 20 µm with 5.22% of Zn grade. In addition to that as a main impurity Si grade of -20 µm size fraction was determined as 21.14% and 11.49% of Si content has particle size less than 20 µm. As was expected, mainly due to the presence of quartz highest grade of Si was observed in coarser fractions. Due to these reasons, desliming process before the flotation does not seem advantageous since nearly 10% of lead and zinc was concentrated in -20 µm size fraction. Apart from these, exclusion of this fraction before the flotation does not provide considerable enrichment in terms of impurities since Si content of the ore sample was concentrated in coarser fractions.

Table 3.4 Elemental Distributions of Representative Sample with respect Different Particle Size

Fraction	Total Weight (g)	Weight (%)	Cum Over Size (%)	Cum Undersize (%)	Pb (%)	Pb Dis. (%)	Zn (%)	Zn Dis. (%)	Fe (%)	Fe Dis. (%)	Al (%)	Al Dis. (%)	Ca (%)	Ca Dis. (%)	Mg (%)	Mg Dis. (%)	Si (%)	Si Dis. (%)
+1.2mm	147.16	19.89	19.89	80.11	2.62	16.93	6.35	19.67	5.24	15.24	3.90	18.09	0.51	14.95	0.45	16.44	26.11	22.43
-1200+850µm	138.50	18.72	38.61	61.39	3.20	19.46	6.38	18.60	5.73	15.68	3.90	17.03	0.5	13.79	0.45	15.47	24.28	19.63
-850+500µm	113.73	15.37	53.98	46.02	3.06	15.28	6.91	16.54	6.46	14.52	3.91	14.02	0.53	12.00	0.48	13.55	23.44	15.56
-500+300µm	104.30	14.10	68.08	31.92	3.51	16.07	7.04	15.45	7.72	15.91	3.94	12.95	0.56	11.63	0.48	12.43	20.60	12.54
-300+150µm	49.43	6.68	74.76	25.24	3.72	8.07	7.29	7.58	8.79	8.59	3.83	5.97	0.74	7.28	0.56	6.87	20.10	5.80
-150+106µm	26.76	3.62	78.37	21.63	3.90	4.58	6.86	3.86	9.08	4.80	3.80	3.21	0.95	5.06	0.70	4.65	20.95	3.27
-106+75µm	23.29	3.15	81.52	18.48	3.70	3.78	6.27	3.07	8.43	3.88	3.63	2.66	0.98	4.55	0.73	4.22	21.62	2.94
-75+53µm	17.66	2.39	83.91	16.09	3.61	2.80	5.86	2.18	7.58	2.65	3.13	1.74	0.96	3.38	0.69	3.03	24.03	2.48
-53+38µm	11.10	1.50	85.41	14.59	3.37	1.64	5.43	1.27	7.19	1.58	3.08	1.08	1.09	2.41	0.69	1.90	24.55	1.59
-38+20µm	14.85	2.01	87.41	12.59	2.84	1.85	4.96	1.55	6.47	1.90	2.83	1.32	0.91	2.69	0.61	2.25	26.25	2.28
-20µm	93.13	12.59			2.33	9.53	5.22	10.23	8.29	15.26	7.47	21.93	1.2	22.26	0.83	19.19	21.14	11.49
Total	**739.91**	**100.00**			**3.08**	**100.00**	**6.42**	**100.00**	**6.84**	**100.00**	**4.29**	**100.00**	**0.68**	**100.00**	**0.54**	**100.00**	**23.16**	**100.00**

In order to perform effective flotation concentration tests and provide sufficient degree of liberation of valuable entities, grinding tests were conducted prior to the flotation tests. According to the mineralogical studies, targeted particle size was determined as less than 75 µm. Grindability tests were performed in order to determine the required grinding duration to reduce particle size of the ore sample to -75 µm from -2mm. Within the scope of this, representative ore samples were subjected to wet grinding tests for 5, 7.5, 10 and 12.5 minutes in a laboratory rod mill in a controlled manner.

Figure 3.28 a) Representation of Rod Mill b) Representation of Grinding Media

During grinding tests previously prepared 400 gr representative ore samples with the particle size -2.00 mm were used. In the context of the tests, a pulp with 60% solid (by weight) was prepared in order to use as feed material. Stainless steel rods were used as the grinding media with different diameters as 9 x 18 mm Ø, 5 x 25 mm Ø, 2 x 38 mm Ø. Particle size distributions of representative ore samples after 5, 7.5, 10 and 12.5 minutes of grinding are presented in Figure 3.30 graphically and Table 3.5-3.8.

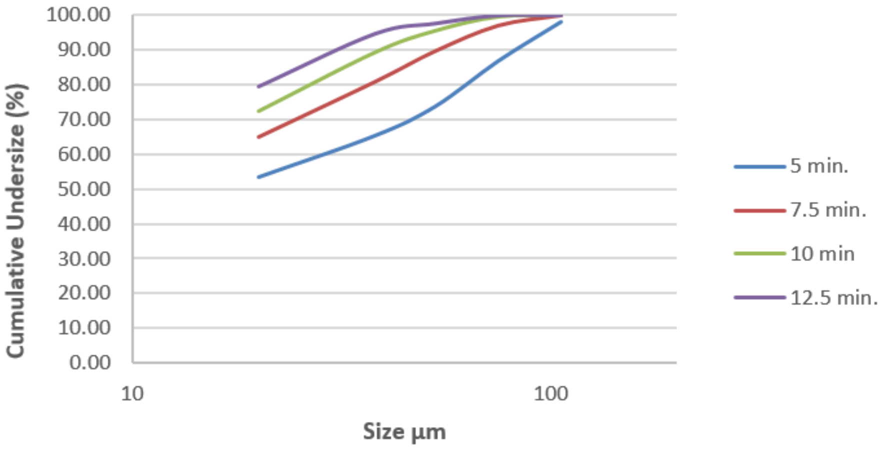


Figure 3.29 Particle Size Distribution of Yozgat-Akdağmadeni Ore with respect to Different Grinding Period

Table 3.5 Particle Size distribution of -2 mm Yozgat – Akdağmadeni Ore after 5 minutes Grinding

Particle Size Fraction	**Weight (%)**	**Cumulative Undersize (%)**
+106µm	1.91	98.09
-106+75µm	11.21	86.88
-75+53µm	13.02	73.86
-53+38µm	8.41	65.45
-38+20µm	11.90	53.55
-20µm	53.55	
Total	100.00	

Table 3.6 Particle size distribution of -2 mm Yozgat – Akdağmadeni Ore after 7.5 minutes Grinding

Particle Size Fraction	**Weight (%)**	**Cumulative Undersize (%)**
+106µm	-	100.00
-106+75µm	2.95	97.05
-75+53µm	7.37	89.68
-53+38µm	8.87	80.81
-38+20µm	15.98	64.84
-20µm	64.84	
Total	100.00	

Table 3.7 Particle size distribution of -2 mm Yozgat – Akdağmadeni Ore after 10 minutes Grinding

Particle Size Fraction	**Weight (%)**	**Cumulative Undersize (%)**
+106µm	-	100.00
-106+75µm	0.40	99.60
-75+53µm	4.07	95.53
-53+38µm	6.27	89.25
-38+20µm	17.02	72.23
-20µm	72.23	
Total	100.00	

Table 3.8 Particle size distribution of -2 mm Yozgat – Akdağmadeni Ore after 12.5 minutes Grinding

Particle Size Fraction	**Weight (%)**	**Cumulative Undersize (%)**
+106µm	-	100
-106+75µm	-	100
-75+53µm	2.32	97.68
-53+38µm	2.96	94.72
-38+20µm	15.18	79.54
-20µm	79.54	
Total	100.00	

According to the above given grinding test results, particle size of the representative samples coarser than 75 µm after grinding for 5 minute is approximately 13% of the sample by weight. However, when the representative sample were subjected to grinding for 7.5 minute, approximately 90% of the ore sample pass under the 75 µm particle size which would provide sufficient degree of liberation for the flotation concentration work. Therefore; the representative feed samples for flotation concentration process were subjected to the grinding for 7.5 min prior to the flotation.

3.2.7. Concentration of Lead by Flotation

In order to obtain a lead concentrate from Yozgat-Akdağmadeni ore, flotation concentration studies were conducted. Within the scope of the flotation studies laboratory scale Denver type flotation machine with one liter cell was utilized. Laboratory scaled flotation machine would be seen in Figure 3.31. Flotation tests were conducted according to batch method by using approximately 400 grams of representative ore samples at 40% solids by weight in the pulp. As it was indicated before, in order to provide sufficient liberation of targeted minerals, representative samples were ground for 7.5 minutes prior to the flotation concentration studies. Test conditions such as conditioning times, reagent dosages and pH were changed by differentiating the operating parameters during the flotation studies. Details of aforementioned parameters at each flotation concentration test could be seen in the Appendix A, pH of the pulp was adjusted by using different types of modifiers such as H_2SO_4 and Na_2CO_3 according to targeted pH value. As it was indicated in literature review of this thesis study, one of the most important parameter in the flotation of carbonaceous lead minerals is the sulfidization in terms of dosage and conditioning time. As one of the common sulfidizer agent for flotation of cerussite, Na_2S was utilized for the activation of lead mineral surfaces. In addition to that, xanthate type collector was used within the scope of flotation studies, as they are the most effective reagents in flotation of oxide minerals while dithiophosphates and merceptants could be utilized as secondary collectors but also based on the contamination originated due to the naturally hydrophobic impurities in the ore, making the utilization of anionic type collector inapplicable (Bulatovic, 2007). As a dispersing agent, sodium silicate (Na_2SiO_3) was used for both depressing Ca, Mg, and Si containing gangue minerals and to supply sufficient degree of liberation by providing the dispersion of the pulp. In order to obtain suitable froth size and strength prior to the aeration, F-533 is utilized as the frother. Chemicals and reagents used during flotation tests are given in the Table 3.9.

Figure 3.30 Laboratory type Denver Flotation Machine

Within the scope of flotation concentration studies, it was expected to recover lead minerals in concentrate and also zinc and remaining impurities are depressed in the tailings fraction.

Table 3.9 Chemicals and reagents used during the flotation experiments of the study

Reagent				
pH Modifiers	**Depressants**	**Collector (promoter)**	**Activator**	**Frother**
Sulfuric Acid (H_sSO_4) (Merck)	Sodium Silicate (Na_2SiO_3) (Merck)	Potassium Amyl Xanthate (PAX)	Sodium sulphide (Na_2S)	F-533 (Cytec)

Consequently, at the end of flotation concentration tests tailing and concentrate fractions were dried in a laboratory furnace at 105 °C ± 5 °C for elemental analysis. Following the drying, products of the flotation studies were weighted and prepared for the ICP-OES analysis. Within the use of elemental analysis results and weight measurements, metallurgical performances of each tests were evaluated in terms of grade and recovery values.

3.2.8. Extraction of Zinc by Leaching

Since the concentration of smithsonite might be challenging by using conventional flotation method, extraction of zinc from smithsonite was performed by utilizing hydrometallurgical methods, so-called leaching. The main motivation of the conducted leaching tests was the selective extraction of zinc from cerussite flotation tailing with maximum grade and recovery values by remaining impurities in the leach residue. Within the context of the leaching tests, three-necked glass flask having volume of 500 ml was used. Condenser was connected with three necked flask in order to prevent evaporation of the leaching solution. Moreover, pH and temperature of the solution was measured along the leaching duration. In order to provide sufficient mixing effect, three necked glass flask was placed on the temperature controlled magnetic stirrer. General view of the leaching test set-up is given in the Figure 3.32. Approximately 20 grams of representative samples prepared from cerussite flotation tailings were used with 1:10 solid to liquid ratio. Temperature of the solution was adjusted to previously determined value and constant temperature values were provided in each leaching test with the help of temperature controlled magnetic stirrer.

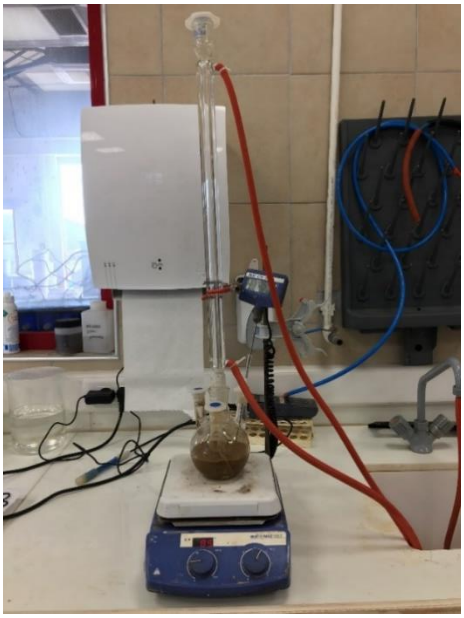


Figure 3.31 Leaching Setup

There are six different leaching lixiviant used within the scope of hydrometallurgical treatment of smithsonite. For the each leaching reagent, 10 leaching tests were conducted with three different parameters as reagent concentration, temperature and leaching time. In this context leaching experiments were designed according to two level full factorial statistical design. In order to construct statistical design, effect of three specified parameters were studied. Tests conditions of leaching studies are given in the Table 3.10.

Table 3.10 Experimental Parameters of Leach Tests

Leaching Reagent	Concentration	Temperature	Leaching Time (min)
Sulfuric Acid	1M, 2M, 3M	30°C, 60°C, 90°C	60, 120, 180
Ammonia	5M, 6M, 7M	25°C, 30°C, 35°C	120, 240, 360
Ammonium Chloride	3M, 4M, 5M	30°C, 60°C, 90°C	60, 120, 180
Ammonium Carbonate	1M, 2M, 3M	30°C, 40°C, 50°C	60, 120, 180
Boric Acid	0.5M, 0.75M, 1M	40°C, 60°C, 80°C	30, 60, 90
Citric Acid	0.5M, 0.75M, 1M	50°C, 70°C, 90°C	60, 90, 120

At the end of each leaching experiment following the recording of the pH and temperature values of the solution solid-liquid separation process was performed by using vacuum filter. Constructed system for solid-liquid separation is presented in Figure 3.33. Following the solid-liquid separation, volume of pregnant solutions were recorded and representative samples were taken in order to perform elemental analysis. In order to recover dissolved metallic entities which might be remained within the leach residue, 2 steps of washing processes were performed. Within the scope of washing steps, wash water with 1:5 solid to liquid ratio was utilized. Washed leach residues were dried in laboratory furnace at 100 °C for further analysis. After drying, the weights of the leach residues were recorded and prepared for the chemical analysis. According to the chemical analysis and measurements, metallurgical balance tables for each test was conducted in order to evaluate leach performance within the consideration of zinc extraction rates. Extraction rate and concentration of zinc in pregnant solution for each experiment will be discussed in result and discussion part of the thesis study. In addition to that, dissolution rates of impurities will also be considered.

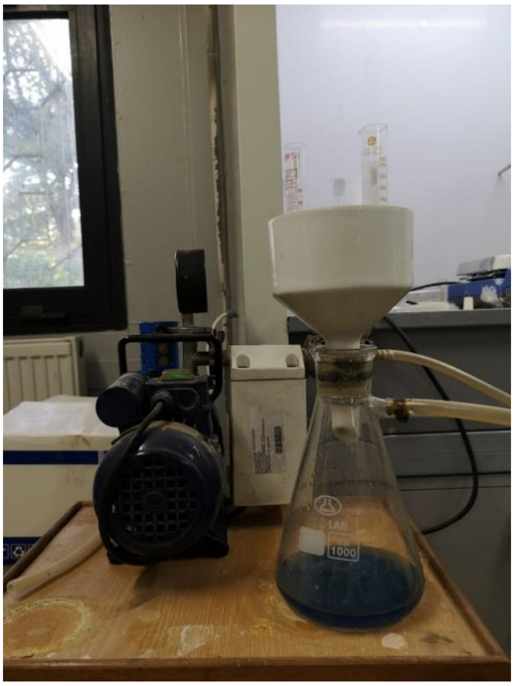


Figure 3.32 Solid-Liquid Separation

The main motivation of this study is developing technically and economically feasible method for the enrichment of Yozgat – Akdağmadeni carbonaceous lead and zinc ore. Consequently, optimum processing flow which presents maximum recovery of valuable metals with reasonable grades consists of two major method namely flotation concentration and leaching. As indicated before, flotation studies were conducted to obtain lead concentrate from run of mine ore by providing selective separation. In addition to these, flotation tailing was exposed to leaching tests in order to obtain selective extraction of zinc with technically and economically feasible way. In this context, proposed flow sheet is given in the Figure 3.34.

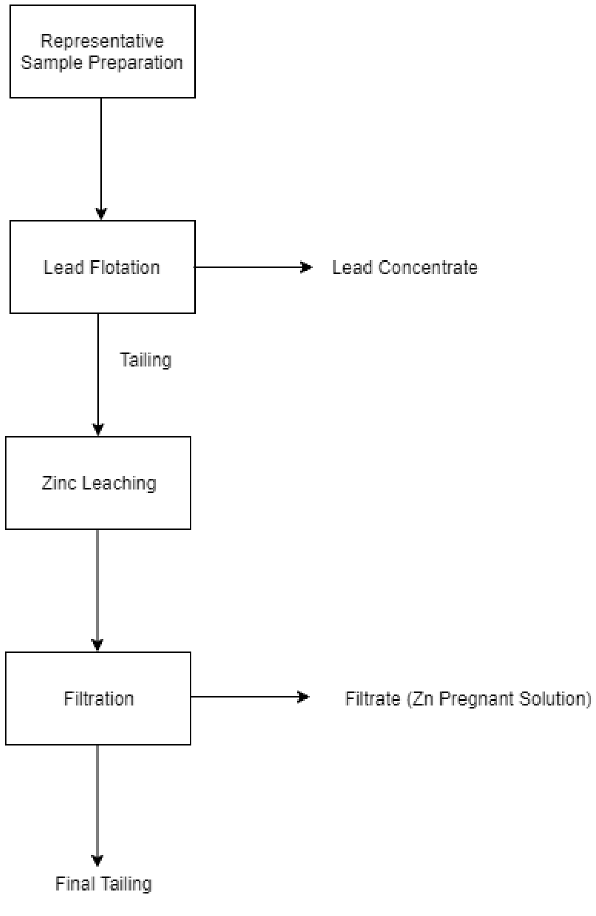


Figure 3.33 Proposed Flowsheet for Enrichment of Yozgat – Akdağmadeni Ore

CHAPTER 4

RESULT AND DISCUSSION

4.1. Flotation of Cerussite

As was indicated in the previous sections, flotation tests were conducted in order to obtain a cerussite concentrate at reasonable grade and recovery values. With the aim of determining the optimum flotation conditions yielding maximum possible recovery and grade, series of flotation test by varying different parameters were performed. According to the information obtained from previous studies and literature review, sulphuric acid was used as the pH regulator, Na_2SiO_3 was used as the dispersant, Na_2S was used as the activator, potassium amyl xanthate (PAX) was used as the collector and F-533 was used as the frother. During the flotation tests variable operational parameters were chosen as sulfidizer dosage, sulfidizer conditioning time, collector dosage and pH. Corresponding effects of each parameter on flotation performance were investigated by changing each of them one by one while keeping rest of all parameters as constant. Within the consideration of low floatability of cerussite mineral, main motivation of the preliminary optimization tests was constructed on obtaining maximum recovery of lead as a pre-concentrate. Grade values of each test will be further improved by subsequent cleaning flotation stages correspondingly.

4.1.1. Effect of Sulfidizer Dosage

Na_2S is one of the most common and effective sulfidizer during cerussite flotation however amount of dosage would be a critical aspect since excessive amount of sulfidizer causes depression of cerussite and contrarily insufficient dosage would not be able to provide required surface activation. In this context, series of flotation tests were conducted in order to define optimum sulfidizer dosage to provide sufficient surface activation for cerussite mineral. Within this context, Na_2S dosage was varied at a pulp pH between 6.5-7.00 by using H_2SO_4 as pH regulator and potassium amyl xanthate (PAX) was used as collector with the quantity of 300g/t by 10 minutes of conditioning time. Na_2SiO_3 was used as depressant in order to provide dispersion of clays from mineral surfaces and depression of gangue minerals, as silicon, with an amount of 250 g/t by 10 minutes of conditioning time. In addition to that, F-533 was utilized as frother with the amount of 75g/t. Conditioning time of sulfidizer was kept constant as 10 minutes. Test conditions are presented in Table 4.1. Metallurgical balance table of the flotation tests, including Pb entities that focused on the effect of sulfidizer dosage is given in the Table 4.2.

Table 4.1 Tests Conditions of Flotation Tests Performed Under Different Activator Dosage

Tests	**pH**	**Activator**	**Activator Dosage**	**Conditioning Time**
1	6.50-7.00	Na_2S	500 g/t	10 min.
2			1000 g/t	
3			1500 g/t	
4			2000 g/t	
5			3000 g/t	
6			4000 g/t	
7			10000 g/t	

Table 4.2 Metallurgical Balance Table with respect to Obtained Lead Concentrate from Rougher Flotation Tests

Tests	**Pb (%)**	**Pb Recovery (%)**
1	4.74	49.31
2	4.68	50.82
3	3.91	55.27
4	5.47	65.48
5	5.56	65.08
6	5.93	72.91
7	7.66	76.98

According to chemical analysis results, metallurgical balance tables were constructed which were also given in Appendix A. In order to determine optimum flotation conditions, firstly there was focused on the recovery of lead entities. As it was expected, it was determined that recovery of cerussite mineral was directly proportional with the activator dosage. In this context, maximum cerussite recovery was observed when Na_2S dosage was kept as 10.000 g/t and conditioned for 10 minutes.

In order to examine effect of Na_2S dosage on the recovery of cerussite, recovery rates were determined as the result of metallurgical balance for each test, which was also investigated individually. Within the scope of Test-1, Na_2S dosage was adjusted at 500g/t which yields very low cerussite recovery as 49.31% and dis not seem to be sufficient in terms of effective lead recovery. Then, in order to enhance cerussite recovery rate of Na_2S dosage was increased to 1000 g/t however, cerussite recovery was not enhanced at reasonable values since it was calculated as 50.82% Pb recovery. Within the context of the Test-3, Na_2S dosage was adjusted as 15000g/t but significant incrementation on cerussite recovery rate couldn’t be obtained since lead recovery was calculated as approximately 55%. Test-4 was conducted by using 2000g/t Na_2S based on the previous studies (Talan, Beneficiation of Oxide Lead and Zinc Mineral by Selective Flotation and Ammonia Leaching, 2016) achieving relatively high recovery rates of cerussite by using 2000g/t Na_2S for similar ore types. However, Akdağmadeni ore did not response well as in previous ones since recovery of cerussite was calculated as 65.48% which is also not acceptable due to the lower recovery of Pb entities and the main focus of the study was obtaining highest possible Pb recovery values. Therefore; activator dosage was increased to 3000g/t within the scope of Test-5, but cerussite recovery rates remained as approximately 65%. Test-6 was performed under the conditions of relatively higher activator dosage as 4000g/t and recovery rates of lead entities was enhanced at a relatively reasonable rates as 72.91%. Within the consideration of possible further cleaning stages to improve grade of the obtained lead concentrate, higher recovery rates were required. In accordance with this purpose, Test-7 was performed by using relatively extreme Na_2S dosage as 10000g/t. As the result of Test-7 recovery rates of lead entities was calculated as approximately 77%

which would be acceptable as reasonable. At this stage, the activator dosage should be evaluated in terms economics, based on the extremely higher consumption. Graphical representation of incrementation on cerussite recovery rate with respect to increasing Na_2S dosage was represented in Figure 4.1.

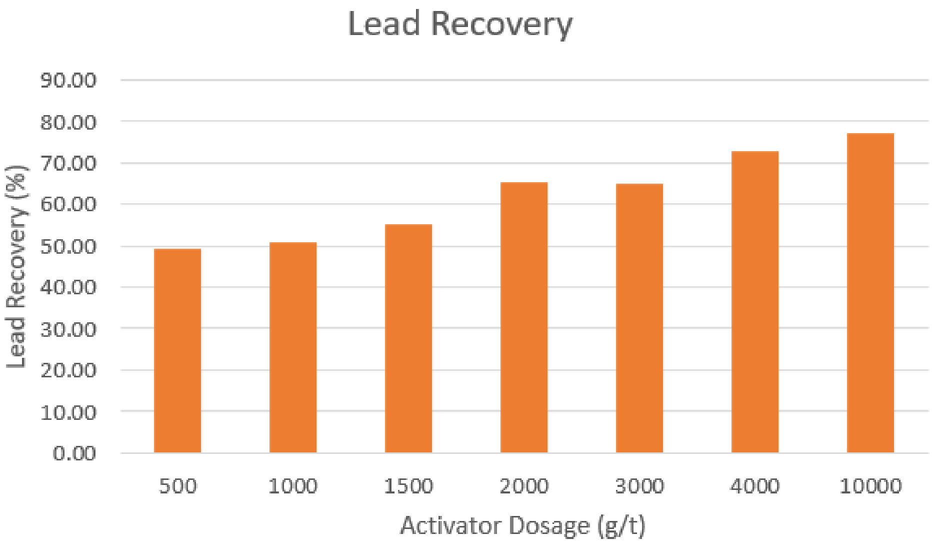


Figure 4.1 Change in Lead Recovery with respect to Activator Dosage

4.1.2. Effect of Sulfidizer Conditioning Time

In order to examine effect of sulfidizer conditioning time on cerussite flotation performance, series of tests were conducted. Within this context, Na_2S conditioning time was varied at a pulp pH of 6.5-7.00 by using H_2SO_4 as pH regulator and potassium amyl xanthate (PAX) was used as collector with the quantity of 300g/t by 10 minutes of conditioning time. Na_2SiO_3 was used as depressant, as silicon, with an amount of 250 g/t by 10 minutes od conditioning time. In addition to that F-533 is utilized as the frother with the amount of 75g/t. Sulfidizer dosage was kept constant as 2000g/t. Test conditions are presented in Table 4.3. Metallurgical balance table of the flotation tests, including Pb entities that focused on the effect of conditioning time of sulfidizer is given in the Table 4.4.

Table 4.3 Tests Conditions of Flotation Tests Performed Under Different Activator Conditioning Time

Tests	pH	Activator	Activator Dosage	Conditioning Time
8	6.50 -7.00	Na_2S	2000 g/t	10 min.
9				15 min.
10				20 min.

Table 4.4 Metallurgical Balance Table with respect to Lead

Tests	Pb (%)	Pb Recovery (%)
8	5.60	64.53
9	4.78	69.19
10	4.60	56.66

In order to make a detailed investigation on the effect of sulfidizer conditioning time on lead recovery rates, three different tests were performed with different conditioning times of activator as 10 minutes, 15 minutes and 20 minutes. The other parameters were kept as constant, as was indicated before. Since Na_2S dosage was adjusted to 2000g/t recovery rates were not calculated as high as it was in Test-7, however results provide opportunity to make comment on the effect of conditioning time of Na_2S on lead recovery rates since the only varying parameter between the three tests were conditioning time of the activator. Test-8 was conducted by exposing ore to Na_2S for 10 minutes and lead recovery rate was calculated as 64.53%. In order to enhance lead recovery rates, conditioning time of Na_2S was increased to 15 minutes from 10 minutes within the context of Test-9. As the result of chemical analysis and metallurgical calculations of lead concentrate obtained from Test-9, lead recovery rate was determined as 69.19%, which could also be determined that increase in conditioning time would help on surface activation of cerussite. In order to investigate further possible incrementation of lead recovery by increasing conditioning time of activator, ore was exposed to Na_2S for 20 minutes, but the lead recovery rate was decreased drastically to 56.66%. This would be resulted from the excessive exposure of Na_2S in terms of conditioning time which might cause depression of cerussite entities. Graphical representation of the effect of Na_2S conditioning time on cerussite recovery is given in Figure 4.2.

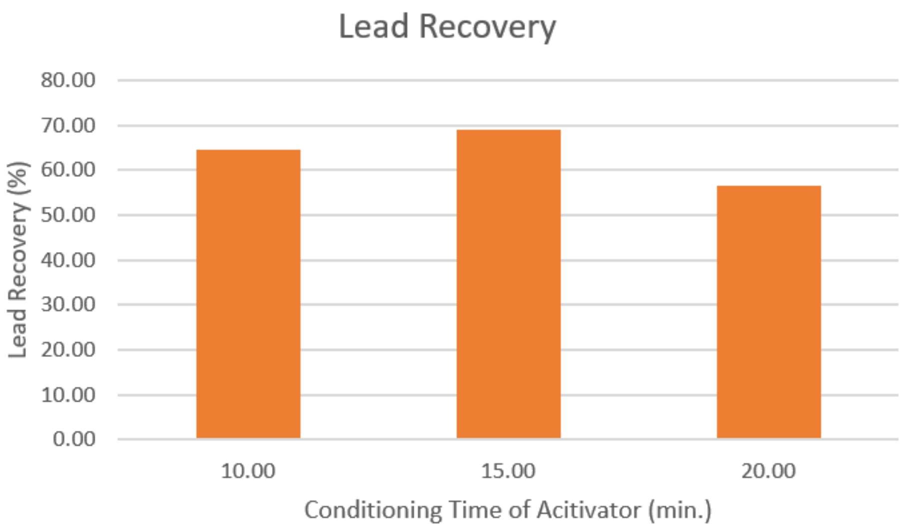


Figure 4.2 Change in Lead Recovery with respect to the Activator Conditioning Time

4.1.3. Effect of Collector Dosage

Series of flotation tests were conducted in order to define the optimum collector dosage to obtain maximum possible recovery of Pb entities. Within this context, PAX dosage was varied at a pulp pH 6.5-7.00 by using H_2SO_4 as pH regulator and Na_2S was used as the collector with the quantity of 2000g/t by 10 minutes of conditioning time. Na_2SiO_3 was used as the depressant within the amount of 250 g/t by 10 minutes of conditioning. In addition to that F-533 is utilized as the frother with the amount of 75g/t. Conditioning time of PAX kept constant as 10 minute. Test conditions and metallurgical results are presented in Table 4.5. Metallurgical balance table of the flotation tests, including Pb entities that focused on the effect of collector dosage is given in the Table 4.6.

Table 4.5 Test Conditions Tests Conditions of Flotation Tests Performed Under Different Collector Dosage

Tests	pH	Collector	Collector Dosage	Conditioning Time
11	6.50 - 7.00	PAX	200 g/t	10 min.
4			300 g/t	
12			400 g/t	
13			500 g/t	

Table 4.6 Metallurgical Balance Table with respect to Lead

Tests	Pb (%)	Pb Recovery (%)
11	4.60	55.67
4	5.47	65.48
12	4.60	64.69
13	5.64	65.92

In order to make detailed investigation on the effect of collector dosage on lead recovery rates, three different tests were performed with different amount of collector dosages as 200g/t, 300 g/t, 400g/t and 500g/t. The other parameters were kept as constant, as was indicated before. Within the scope of these flotation tests, recovery rates were not obtained as high as possible to achieve maximum lead recovery rates however they are enough to give reliable information to examine cerussite flotation behavior by varying collector dosage. In this context, Test-11 was performed by using 200g/t PAX and lead recovery rate was calculated as 55.67% while lead recovery rates was increased to 64.69% when the collector dosage was increased to 400 g/t within the scope of Test-12. In addition, as the result of the Test-13 conducted by using 500g/t PAX in order to observe whether the collector affects the flotation performance on lead recovery rates in the case of further incrementation PAX dosage, it was seen that lead recovery rate was obtained as 65.92% which was not much differentiated with previously conducted Test-12. Graphical representation of cerussite recovery rate with respect to increasing collector dosage was represented in Figure 4.3.

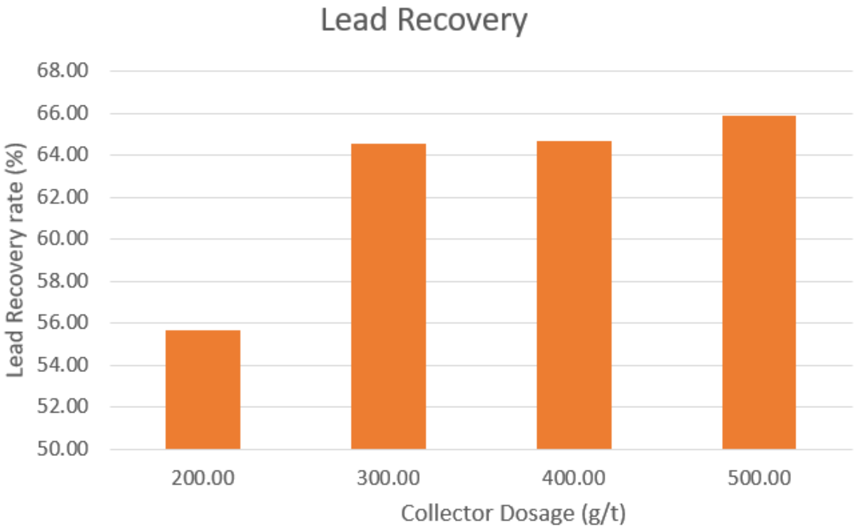


Figure 4.3 Change in Lead Recovery with respect to Collector Dosage

4.1.4. Effect of pH

In order to investigate the effect of pulp pH on cerussite flotation, two flotation tests were performed under alkali and slightly acidic conditions. H_2SO_4 was as used as pH regulator and potassium amyl xanthate was used as the collector with the dosage of 300 g/t by 10 minutes of conditioning time. Na_2S was used as the activator within the quantity of 2000g/t and conditioned for 10 minutes. Na_2SiO_3 was used as the depressant with the amount of 250 g/t by 10 minutes of conditioning. In addition to that F-533 is utilized as the frother within the amount of 75g/t. Test conditions are presented in Table 4.7. Metallurgical balance table of the flotation tests, including Pb entities that focused on the effect of pulp pH is given in the Table 4.8.

Table 4.7 Tests Conditions of Flotation Tests Performed under Different pH Value

Tests	**pH**	**Activator**	**Activator Dosage**	**Conditioning Time**
14	6.50	Na_2S	2000 g/t	10 min.
15	9.00			

Table 4.8 Metallurgical Balance Table with respect to Lead

Tests	**Pb (%)**	**Pb Recovery (%)**
14	5.32	66.92
15	5.56	50.57

As it was indicated in Literature Review section, there was different successful studies conducted under both alkali and acidic conditions. Under slightly acidic conditions (pH = 6.5) and recovery rate of lead entities was calculated as approximately 67% while pH was adjusted to alkali conditions lead recovery rate was decreased to 50.57%. In the light of these results, it would be inferred that Akdağmadeni ore floatability enhances under slightly acidic conditions. Graphical representation of change in cerussite recovery rate with respect to pH value of the pulp was represented in Figure 4.5.

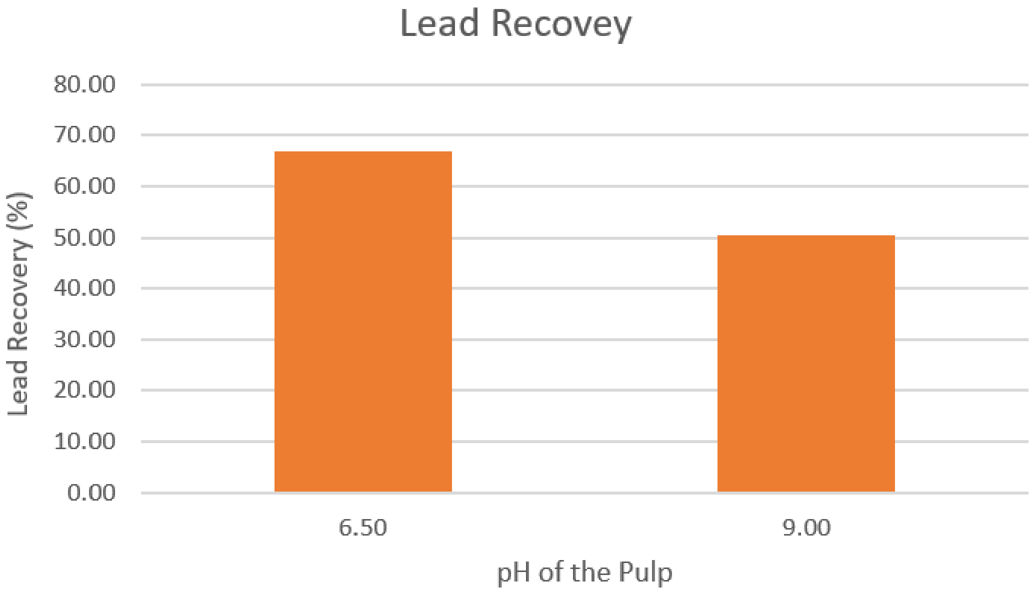


Figure 4.4 Change in Lead Recovery with respect to pH of the Pulp

4.1.5. Optimum Flotation Test

In accordance with the conducted flotation tests, optimum flotation conditions were determined to obtain lead concentrate at maximum possible recovery and grade values. In order to enhance the grade of cerussite to the reasonable levels, 3 stages of cleaning flotation tests were performed without additional reagent usage. Rougher flotation was performed under slightly acidic conditions by using H_2SO_4 as the pH regulator and 250g/t Na_2SiO_3 as the dispersant for 10 minutes of conditioning. Within the scope of optimum flotation tests, 4000 g/t Na_2S was used since there was not defined any significant difference between recovery values obtained from flotation test conducted by using 4000 g/t Na_2S and 10000 g/t Na_2S. Therefore, within the consideration of both technical and economical feasibility, 4000 g/t Na_2S was used. In addition to that, since 15 minutes of conditioning time for sulfidizer provide maximum recovery in lead concentrate during previous flotation tests, Na_2S conditioning time was chosen as 15 minutes. PAX was used as the collector with the amount of 500 g/t which provided maximum recovery according to the conducted tests under variable collector dosage. PAX was conditioned for 10 minutes and followingly 75 g/t F-533 was added to the pulp in order to provide stable froth phase. According to the chemical analysis of the flotation products, final concentrate was obtained with 60.20% Pb grade with 64.29% Pb recovery. Detailed metallurgical balance table belongs to the optimum flotation test was given in the Appendix A. Metallurgical balance table of optimum flotation tests with respect to lead is given in the Table 4.9.

Table 4.9 Metallurgical Balance Table of Optimum Flotation Tests with respect to Lead

Fraction	**Pb (%)**	**Pb Rec. (%)**
Pb Concentrate	60.20	64.29
Cleaner Tailing-3	4.50	5.79
Cleaner Tailing -2	1.02	2.18
Cleaner Tailing -1	0.60	4.37
Final Flotation Tailing	1.05	23.37
Total	2.94	100.00

4.2. Leaching of Zinc

The main motivation of the conducted leaching tests was the selective extraction of zinc from cerussite flotation tailing with maximum recovery value by remaining impurity containing entities in the leach residue. In accordance with this purpose, six different leaching reagents were utilized as sulphuric acid, ammonia, ammonium carbonate, ammonium chloride, boric acid and citric acid. Within this scope, experimental parameters were optimized based on the two level full factorial statistical design and types of the parameters and their ranges to be used in the experimental design were determined according to the data gained from the literature survey and previous studies mentioned in the Literature Survey section of the present study. As it was indicated before, reagent concentration, temperature and leaching time were chosen as the most crucial parameters having significant impact on the results of experiments. In this context, series of experiments were conducted; by varying these parameters within a certain range and their effects on the results of the experiments were evaluated statistically. Leaching tests by using different leaching reagents were conducted while one parameter was varied and the other two parameters were fixed. In this way, interactions between the parameters were also evaluated in details by the constructed statistical model. In addition to the extraction ratio of zinc, removal of impurities were also be considered while evaluating the each parameter and experimental results. Statistical model and final equation of leaching tests were constructed according to the coded factors by using software namely Statease Design Expert. Performance and effectiveness of each leaching reagent according to their capability to extract zinc and reject main impurities such as Fe and Si evaluated with the help of outputs of the software. Detailed metallurgical balance tables of each leaching experiments are given in the Appendix B.

4.2.1. Sulfuric Acid Leaching

Operational parameters of sulphuric acid leaching tests were optimized in order to achieve maximization of zinc extraction and minimization of dissolution of main impurities as Fe and Si. The main motivation of the leaching tests were to obtain a pregnant leach solution enriched in terms of zinc content within minimum amount of impurities. In accordance with this purpose, experimental parameters were optimized by using two level full factorial statistical design. As was indicated before, acid concentration, temperature and leaching time were chosen as variable operational parameters in leaching tests. According to chemical analysis of the leach residues maximum and minimum extraction ratio of the zinc were determined as 99.91% and 96.47% respectively. In addition to that maximum and minimum extraction ratios of the Fe and Si is obtained as 33.83% (Fe) and 96.44% (Fe), 8.81% (Si) and 17.46% (Si). Parameter codes and assigned values for sulphuric acid leaching and target of the experiment are given in the Table 4.10.

Table 4.10 Parameter Codes and Assigned Values for Sulphuric Acid Leaching

Name	Goal	Lower Limit	Upper Limit
A:Concentration	In range	1 M	3 M
B:Temperature	In range	30 C°	90 C°
C:Time	In range	60 min.	180 min.
Zn Rec. (%)	Maximize	96.47	99.91
Fe Rec. (%)	Minimize	33.83	96.44
Si Rec. (%)	Minimize	8.81	17.46

According to evaluation of the results, direct effect and effects of interaction between the operational parameters on zinc extraction, iron dissolution and silicon dissolution were determined. Within this scope, coefficient factor of each parameter on its own and interrelation between these parameters were specified. In addition to that, regression model equations for zinc extraction, iron dissolution and silicon dissolution were constructed by using these coefficients. Factors and corresponding effect on each responses in the Table 4.11.

Table 4.11 Factors and Corresponding Effect on Zinc Extraction Ratio related with Sulphuric Acid Leaching

Factor	**Effect on Zinc Extraction (%)**	**Effect on Iron Dissolution (%)**	**Effect on Silica Dissolution (%)**
A-Concentration (M)	0.19	3.66	-0.77
B-Temperature (C°)	1.43	25.95	1.45
C-Time (min)	0.22	3.83	-0.77
AB	-0.096	- 0.49	1.45
AC	0.071	- 0.079	-0.77
BC	-0.17	- 1.61	1.45
ABC	-0.12	- 2.58	-0.77

Constructed regression equations models for each response were given in the below;

Zinc Extraction (%) = $+98.54 + 0.19\times A + 1.43\times B + 0.22\times C - 0.096\times AB + 0.071\times AC - 0.17\times BC - 0.12\times ABC$

Iron Dissolution (%) = $+68.51 + 3.66\times A + 25.95\times B + 3.83\times C - 0.49\times AB - 0.079\times AC - 1.61\times BC - 2.58\times ABC$

Silica Dissolution (%) = $+13.77 - 0.36\times A + 0.27\times B - 0.11\times C - 1.16\times AB - 2.07\times AC - 0.77\times BC + 1.45\times ABC$

As it would be inferred from the equations the most significant parameter in zinc extraction and iron dissolution is temperature. In addition to that, iron dissolution rate is affected by interaction between three operational parameters and leaching time slightly. Dissolution ratio of silica by using sulphuric acid present differences according to interrelation between three operational factors and concentration-leaching time combination. 3D response graphs presenting relationship between operational parameters and the responses are presented in Figure 4.5- 4.7.

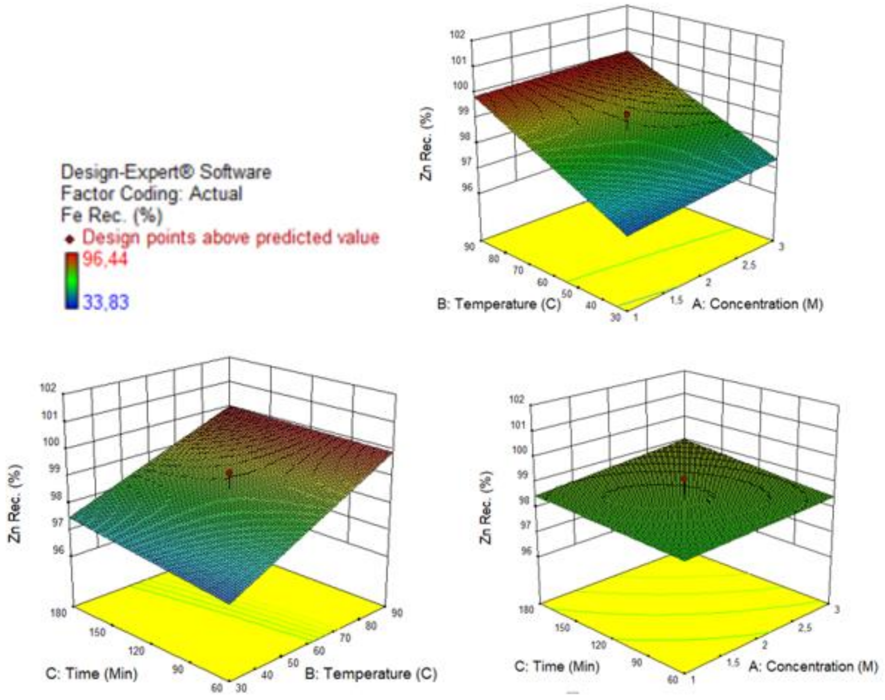


Figure 4.5 3-D Graphical Representation Change in Zinc Extraction Ratio by using Sulphuric Acid with respect to Three Operational Parameters and to Their Combination.

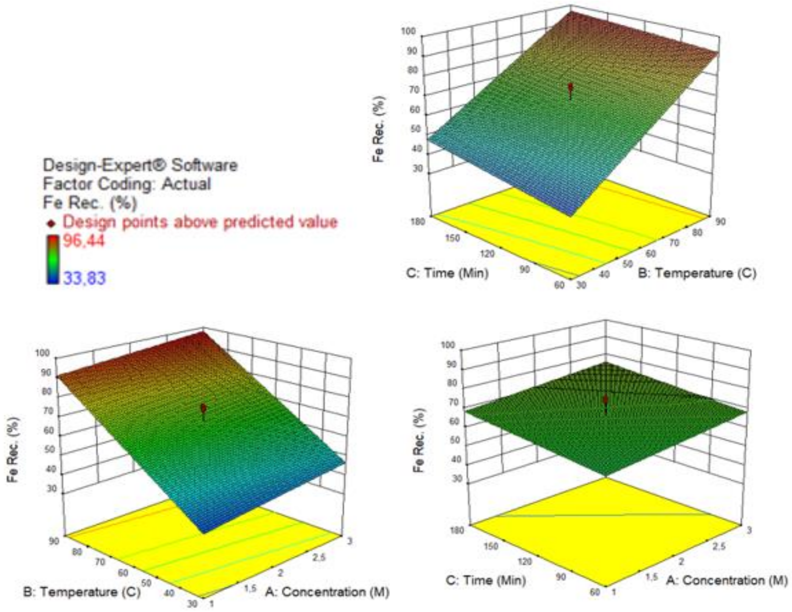


Figure 4.6 3-D Graphical Representation Change in Iron Dissolution Ratio by using Sulphuric Acid with respect to Three Operational Parameters and to Their Combination.

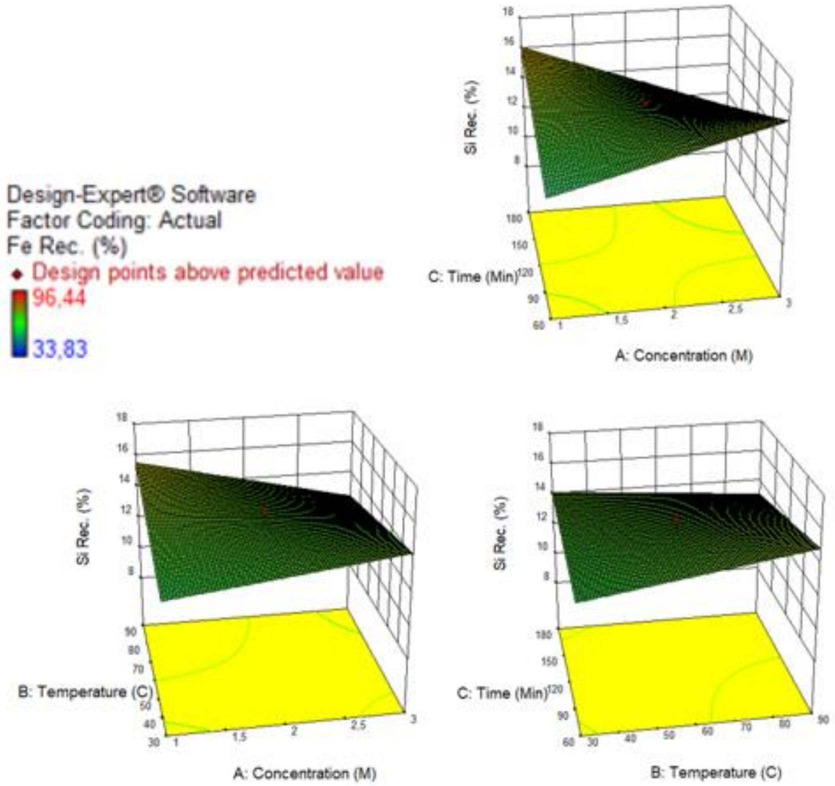


Figure 4.7 3-D Graphical Representation Change in Silica Dissolution Ratio by using Sulphuric Acid with respect to Three Operational Parameters and to Their Combination.

In consideration of the 3-D graphical representations belongs to relationship between three responses and operational parameters, results presents coherence with conducted equations since zinc recovery varies significantly according to change in temperature which also plays important role in dissolution of iron. In addition to that, leaching time and acid concentration have small impact on iron dissolution. Within the consideration of silica dissolution, interrelation between acid concentration and leaching time is the most significant factor. Under the leaching conditions of high acid concentration and longer duration, dissolution of Si decreases. As the result of the conducted evaluation by using Design Expert program optimum leaching test using sulphuric acid has been determined by considering maximum zinc extraction ratio and minimum dissolution rates of Fe and Si. Determined optimum operational parameters are 1M sulphuric acid concentration, 30°C temperature and 60 min leaching time that yielding 96.63% zinc extraction rate, 385.47% iron dissolution rate and 8.52% silica dissolution rate. Output of the software presenting optimum test conditions is given in the Table 4.12.

Table 4.12 Optimum Test Conditions Determined by the Program for Sulphuric Acid Leaching

Test Conditions			**Extraction Rates**		
Reagent Concentration	**Temperature (C°)**	**Leaching Time (min.)**	**Zn (%)**	**Fe (%)**	**Si (%)**
1M	30	60	96.63	35.47	8.52

4.2.2. Ammonia Leaching

Operational parameters of ammonia leaching were optimized in order to achieve maximization of zinc extraction and minimization of dissolution of main impurities as Fe and Si. The main motivation of the leaching tests were to obtain pregnant leach solution enriched in terms of zinc content with minimum amount of impurities. In accordance with this purpose, experimental parameters were optimized by using two level full factorial statistical design. As was indicated before, ammonia concentration, temperature and leaching time were chosen as variable operational parameters in leaching tests. According to chemical analysis of the leach residues maximum and minimum extraction ratio of the zinc are determined as 83.57% and 70.93% respectively. In addition to that maximum and minimum extraction ratios of the Fe and Si is obtained as 12.67% (Fe) and 3.33% (Fe), 14.16% (Si) and 29.18% (Si). Parameter codes and assigned values for ammonia leaching and target of the experiment are given in the Table 4.13.

Table 4.13 Parameter Codes and Assigned Values for Ammonia Leaching

Name	**Goal**	**Lower Limit**	**Upper Limit**
A:Concentration (M)	is in range	5	7
B:Temperature (C°)	is in range	25	35
C:Time (min.)	is in range	120	360
Zn Rec. (%)	maximize	7.93	83.57
Fe Rec. (%)	minimize	3.33	12.67
Si Rec. (%)	minimize	14.16	29.18

According to evaluation of the results, direct effects and effects of interaction between the operational parameters on zinc extraction, iron dissolution and silicon dissolution are determined. Within this scope, coefficient factor of each parameter on its own and interrelation between these parameters were specified. In addition to that, regression model equations for zinc extraction, iron dissolution and silicon dissolution were constructed by using these coefficients. Factors and corresponding effect on each responses in the Table 4.14.

Table 4.14 Factors and corresponding effect on Each Responses related with Ammonia Leaching

Factor	**Effect on Zinc Extraction (%)**	**Effect on Iron Dissolution (%)**	**Effect on Silica Dissolution (%)**
A-Concentration (M)	2.15	- 0.25	- 0.74
B-Temperature (C°)	0.59	- 0.37	0.30
C-Time (min.)	3.53	1.40	1.45
AB	- 0.059	- 1.81	3.96
AC	- 2.08	- 1.61	1.35
BC	0.65	1.21	1.02
ABC	0.051	0.18	1.46

Constructed regression equations models according to coded factors for each response were given in the below;

Zinc Extraction (%) = $+79.35 + 2.15 \times A + 0.59 \times B + 3.53 \times C - 0.059 \times AB - 2.08 \times AC + 0.65 \times BC + 0.051 \times ABC$

Iron Dissolution (%) = +6.45 – 0.25×A – 0.37×B + 1.40×C – 1.81×AB – 1.61×AC + 1.21×BC + 0.18 ×ABC

Silica Dissolution (%) = +21.21 – 0.74×A + 0.30×B + 1.45×C + 3.96×AB + 1.35×AC + 1.02×BC +1.46×ABC

As it would be inferred from the equations the most significant parameter in zinc extraction is ammonia concentration. In addition to that interrelation between ammonia concentration and leaching time have inverse effect on extraction ratio of zinc. In details, dissolution rate of iron effected inversely from the interrelation between ammonia concentration – temperature and ammonia concentration – leaching time. Moreover, relation between temperature and leaching time have direct effect on iron dissolution rate. Within the consideration of silica dissolution the most effective impact is change in combination of ammonia concentration and temperature. 3D response graphs presenting relationship between operational parameters and responses are presented in Figure 4.8- 4.10.

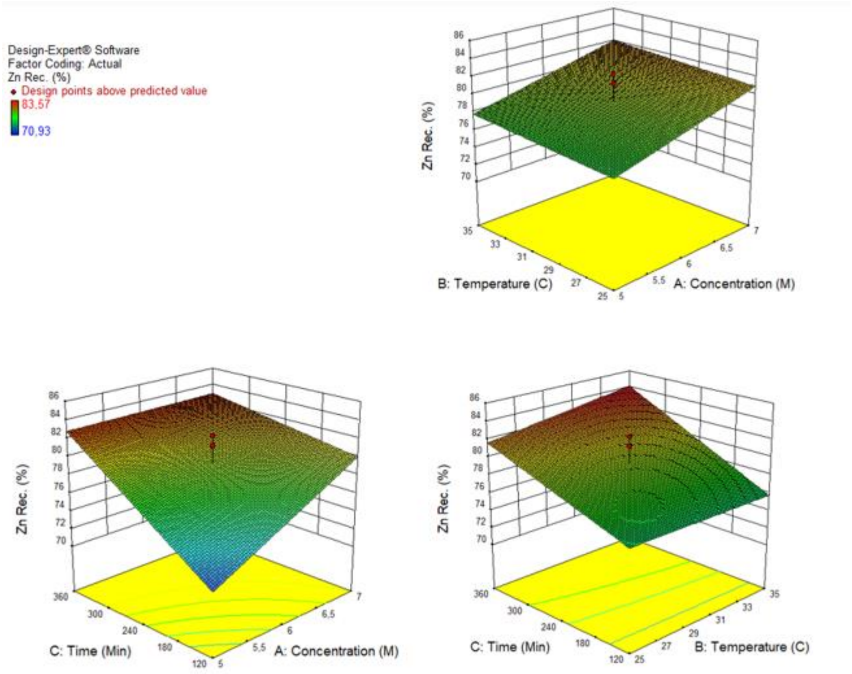


Figure 4.8 3-D Graphical Representation Change in Zinc Extraction Ratio by using Ammonia with respect to Three Operational Parameters and to Their Combination.

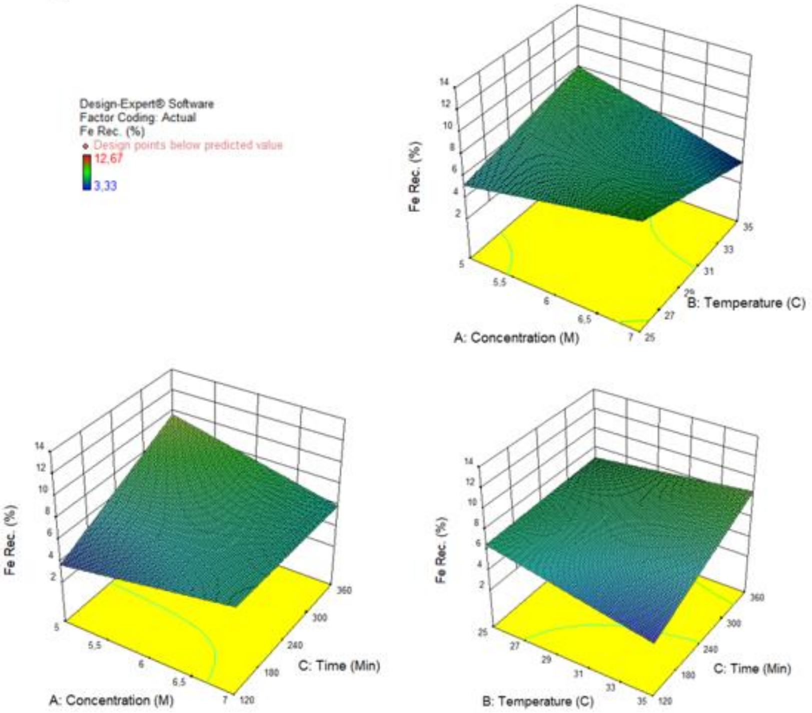


Figure 4.9 3-D Graphical Representation Change in Iron Extraction Ratio by using Ammonia with respect to Three Operational Parameters and to Their Combination.

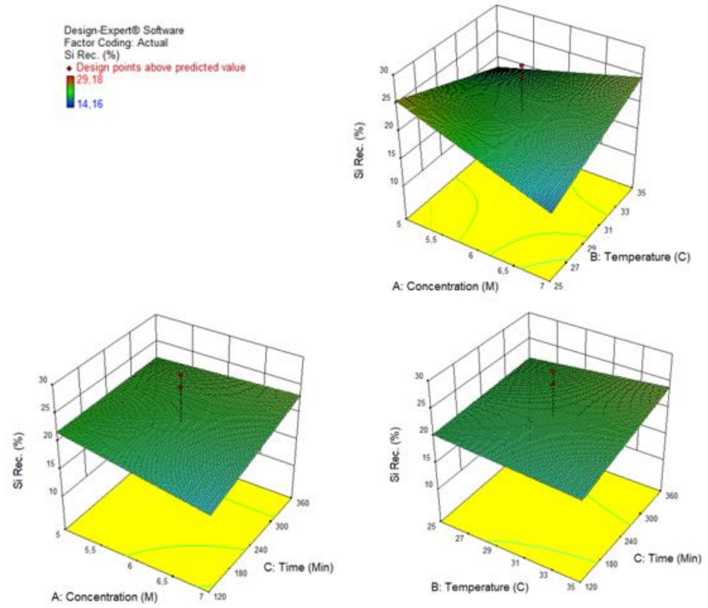


Figure 4.10 3-D Graphical Representation Change in Silica Extraction Ratio by using Ammonia with respect to Three Operational Parameters and to Their Combination.

In consideration of the 3-D graphical representations belongs to relationship between three responses and operational parameters, results presents coherence with the conducted equations since zinc recovery varies significantly according to ammonia concentration and leaching time. In addition to that dissolution of iron varies according to ammonia concentration and leaching time significantly. Within the consideration of silica dissolution, interrelation between temperature and ammonia concentration is the most significant factor. As the result of conducted evaluation by using Design Expert program optimum leaching test using ammonia has been determined by considering maximum zinc extraction ratio and minimum dissolution rates of Fe and Si. Determined optimum operational parameters are 7M ammonia concentration, 25°C temperature and 360 min leaching time yielding 81.73% zinc extraction rate, 6.79% iron dissolution rate and 16.52% silica dissolution rate. Output of the software presenting optimum test condition is given in the Table 4.15.

Table 4.15 Optimum test Conditions Determined by the Program for Ammonia Leaching

Test Conditions			**Extraction Rates**		
Reagent Concentration	**Temperature (C°)**	**Leaching Time (min.)**	**Zn (%)**	**Fe (%)**	**Si (%)**
7M	25	360	81.73	6.79	16.52

4.2.3. Ammonium Chloride Leaching

Operational parameters of ammonium chloride leaching were optimized in order to achieve maximization of zinc extraction and minimization of dissolution of main impurities as Fe and Si. The main motivation of the leaching tests were to obtain pregnant leach solution enriched in terms of zinc content with minimum amount of impurities. In accordance with this purpose, experimental parameters were optimized by using two level full factorial statistical design. As indicated before, ammonium chloride concentration, temperature and leaching time were chosen as variable operational parameters in leaching tests. According to chemical analysis of the leach residues maximum and minimum extraction ratio of the zinc are obtained as 87.81%

and 1.05% respectively. In addition to that maximum and minimum extraction ratios of the Fe and Si is obtained as 12.69% (Fe) and 8.24% (Fe), 20.63% (Si) and 8.8% (Si). Parameter codes and assigned values for ammonium chloride leaching and target of the experiment are given in the Table 4.16.

Table 4.16 Parameter Codes and Assigned Values for Ammonium Chloride Leaching and Target of the Experiment

Name	**Goal**	**Lower Limit**	**Upper Limit**
A:Concentration (M)	is in range	3	5
B:Temperature (C°)	is in range	30	90
C:Time (min.)	is in range	60	180
Zn Rec. (%)	maximize	1.05	87.81
Fe Rec. (%)	minimize	8.24	12,69
Si Rec. (%)	minimize	8.8	20.63

According to evaluation of the results, direct effect and effects of interaction between the operational parameters on zinc extraction, iron dissolution and silicon dissolution are determined. Within this scope, coefficient factor of each parameter on its own and interrelation between these parameters were specified. In addition to that, regression model equations for zinc extraction, iron dissolution and silicon dissolution were constructed by using these coefficients. Factors and corresponding effect on each responses in the Table 4.17.

Table 4.17 Factors and Corresponding Effect on Each Responses related with Ammonium Chloride Leaching

Factor	**Effect on Zinc Extraction (%)**	**Effect on Iron Dissolution (%)**	**Effect on Silica Dissolution (%)**
A-Concentration (M)	6.20	0.34	- 0.14
B-Temperature (C°)	36.30	0.038	1.19
C-Time (min.)	– 0.98	- 0.75	- 0.14
AB	– 0.69	0.65	1.19
AC	– 5.94	- 0.68	- 0.14
BC	5.20	- 0.26	1.19
ABC	1.85	- 0.25	- 0.14

Constructed regression equations models according to coded factors for each response were given in the below;

Zinc Extraction (%) = $+45.72 + 6.20\times A + 36.30\times B - 0.98\times C - 0.69\times AB - 5.94\times AC + 5.20\times BC + 1.85\times ABC$

Iron Dissolution (%) = $+9.97 + 0.34\times A + 0.038\times B - 0.75\times C + 0.65\times AB - 0.68\times AC - 0.26\times BC - 0.25\times ABC$

Silica Dissolution (%) = $+15.13 + 0.46\times A - 1.67\times B + 2.87\times C - 1.08\times AB + 0.30\times AC - 0.14\times BC + 1.19\times ABC$

Within the consideration of determined equations extraction ratio of zinc greatly affected from temperature. In addition to that interrelation between reagents concentration-leaching time and temperature-leaching time have considerable effect on dissolution of zinc by using ammonium chloride solution. Dissolution rate of iron presents relevancy with interrelation of operational parameters. While ammonium chloride concentration-leaching time, temperature-leaching time, ammonium chloride concentration-temperature- leaching time interactions having positive effect on iron removal, interrelation between ammonium chloride concentration and temperature enhances dissolution of iron. Moreover, as a major impurity silica dissolution rates directly proportional with leaching time. It was also affected from interrelation between ammonium chloride concentration and temperature inversely. 3D response graphs presenting relationship between operational parameters and three targeted responses indicated before are presented in Figure 4.11- 4.13.

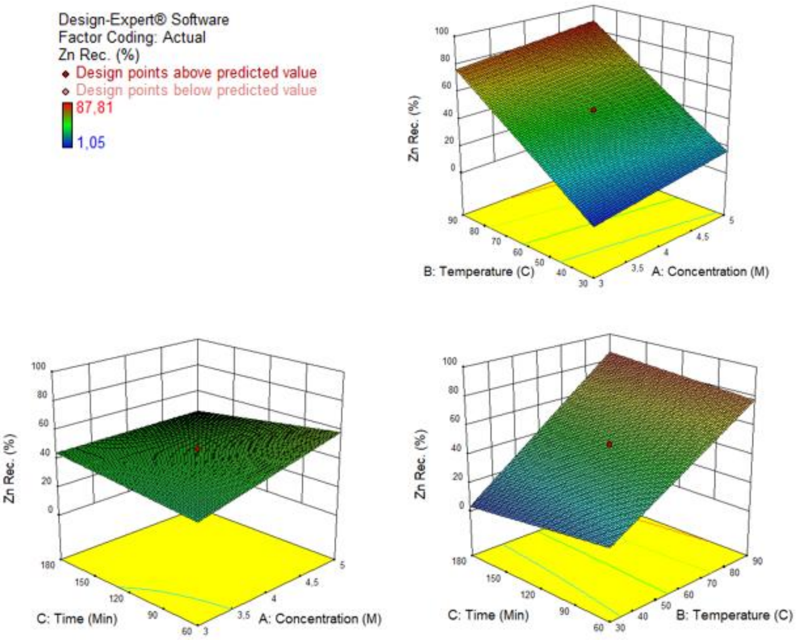


Figure 4.11 3-D Graphical Representation Change in Zinc Extraction Ratio by using Ammonium Chloride with respect to Three Operational Parameters and to Their Combination.

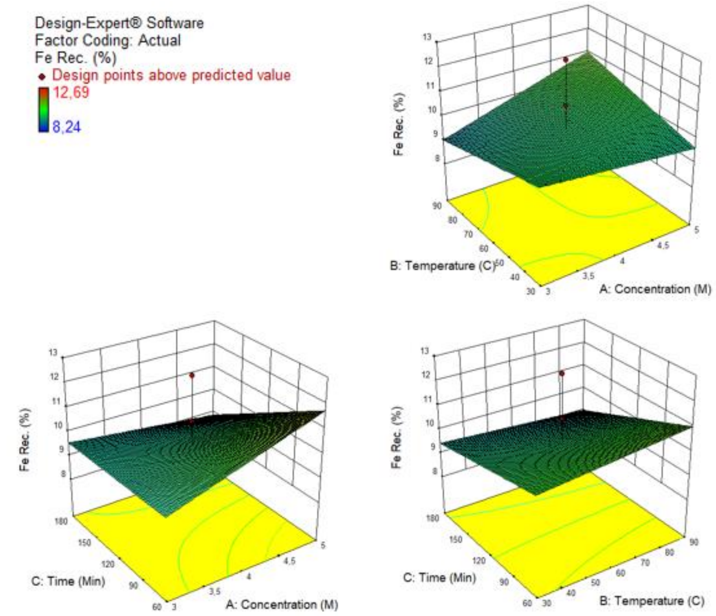


Figure 4.12 3-D Graphical Representation Change in Silica Dissolution Ratio by using Ammonium Chloride with respect to Three Operational Parameters and to Their Combination.

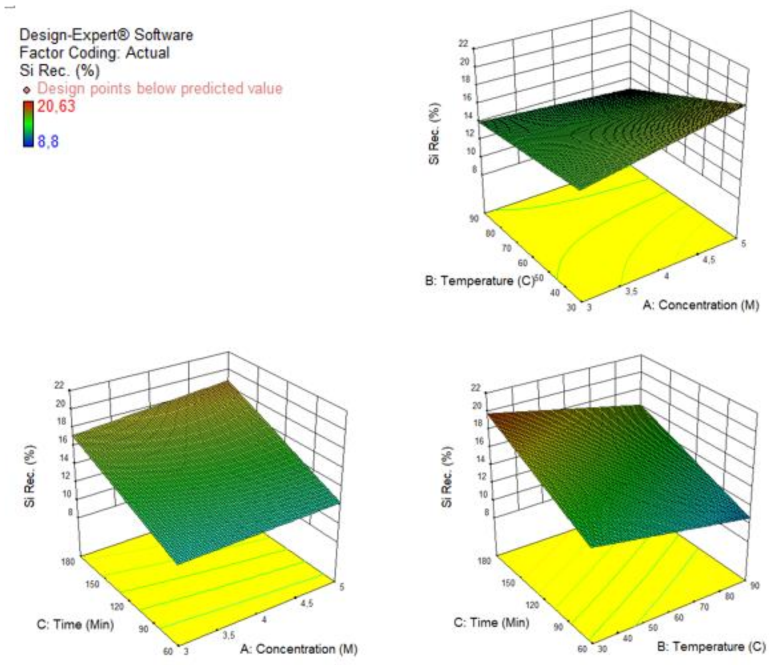


Figure 4.13 3-D Graphical Representation Change in Silica Dissolution Ratio by using Ammonium Chloride with respect to Three Operational Parameters and to Their Combination.

As it would be inferred from the 3-D graphical representations, most significant operational parameter in zinc extraction ratio is temperature. Increasing temperature enhances dissolution of zinc within the ammonium chloride solution. In addition to that interrelation between leaching time and ammonium chloride concentration also affects zinc extraction performance of ammonium chloride leaching. Dissolution rate of iron present variances predominantly according to the interrelation between leaching time and ammonium chloride concentration. As a major impurity silica rejection is one of the most important target of the experiments. The most significant operational parameter on silica dissolution rate is leaching time. As a result of conducted evaluation by using Design Expert program optimum leaching test using ammonium chloride has been determined by considering maximum zinc extraction ratio and minimum dissolution rates of Fe and Si. Determined optimum operational parameters are 5M (4.873) ammonium chloride concentration, 90°C temperature and 60 min leaching time that yielding 86.17% zinc extraction rate, 12.69% iron dissolution rate and 8.89% silica dissolution rate. Output of the software presenting optimum test condition is given in the Table 4.18.

Table 4.18 Optimum Test Conditions Determined by the program for Ammonium Chloride Leaching

Test Conditions			**Extraction Rates**		
Reagent Concentration	**Temperature (C°)**	**Leaching Time (min.)**	**Zn (%)**	**Fe (%)**	**Si (%)**
5M	90	60	86.17	12.69	8.89

4.2.4. Citric Acid Leaching

Operational parameters of citric acid leaching were optimized in order to achieve maximization of zinc extraction and minimization of dissolution of main impurities as Fe and Si. The main motivation of the leaching tests were to obtain pregnant leach solution enriched in terms of zinc content with minimum amount of impurities. In accordance with this purpose, by using two level full factorial statistical design experimental parameters were optimized. As indicated before, ammonium chloride concentration, temperature and leaching time were chosen as variable operational parameters in leaching tests. According to chemical analysis of the leach residues maximum and minimum extraction ratio of the zinc are obtained as 96.84% and 52.43% respectively. In addition to that maximum and minimum extraction ratios of the Fe and Si is obtained as 49.86% (Fe) and 7.93% (Fe), 16.26% (Si) and 1.8% (Si). Parameter codes and assigned values for citric acid leaching and target of the experiment are given in the Table 4.19.

Table 4.19 Parameter Codes and Assigned Values for Citric Acid Leaching

Name	**Goal**	**Lower Limit**	**Upper Limit**
A:Concentration (M)	is in range	0.5	1
B:Temperature (C°)	is in range	50	90
C:Time (min.)	is in range	60	120
Zn Rec. (%)	maximize	5.43	96.84
Fe Rec. (%)	minimize	7.93	49.86
Si Rec. (%)	minimize	1.8	16.26

According to evaluation of the results, direct effect and effects of interaction between the operational parameters on zinc extraction, iron dissolution and silicon dissolution are determined. Within this scope, coefficient factor of each parameter on its own and interrelation between these parameters were specified. In addition to that, regression model equations for zinc extraction, iron dissolution and silicon dissolution were constructed by using these coefficients. Factors and corresponding effect on each responses in the Table 4.20.

Table 4.20 Factors and Corresponding Effect on Each Responses related with Citric Acid Leaching

Factor	Effect on Zinc Extraction (%)	Effect on Iron Dissolution (%)	Effect on Silica Dissolution (%)
A-Concentration (M)	4.86	0.47	2.31
B-Temperature (C°)	15.58	+ 18.30	4.11
C-Time (min.)	1.15	+ 0.13	- 0.24
AB	- 3.84	- 1.34	0.46
AC	- 1.16	0.20	- 082
BC	- 0.29	- 0.069	+ 1.62
ABC	0.62	1.25	0.15

Constructed regression equations models according to coded factors for each response were given in the below;

Zinc Extraction (%) = +82.30 + 4.86×A + 15.58×B + 1.15×C – 3.84×AB – 1.16×AC – 0.29×BC + 0.62×ABC

Iron Dissolution (%) = +29.70 + 0.47×A + 18.30×B + 0.13×C – 1.34×AB + 0.20×AC – 0.069×BC +1.25 ×ABC

Silica Dissolution (%) = +7.45 + 2.31×A + 4.11×B – 0.24×C + 0.46×AB – 0.82×AC + 1.62×BC + 0.15×ABC

Within the scope of constructed equations, it would be inferred that zinc extraction ratio predominantly affected from temperature. Increase in temperature supports extraction ratio of zinc in citric acid solution. In addition to that extraction ratio of zinc inversely proportional with interrelations between citric acid concentration-temperature and citric acid concentration-leaching time. Dissolution rate of iron also increases with increase in temperature. Moreover, interrelation between citric acid concentration and temperature slightly effect rejection rate of iron. Temperature is the most critical operational parameter also for silica dissolution rate. Increasing temperature results with low silica rejection. 3D response graphs presenting relationship between operational parameters and three targeted responses indicated before are presented in Figure 4.14- 4.16.

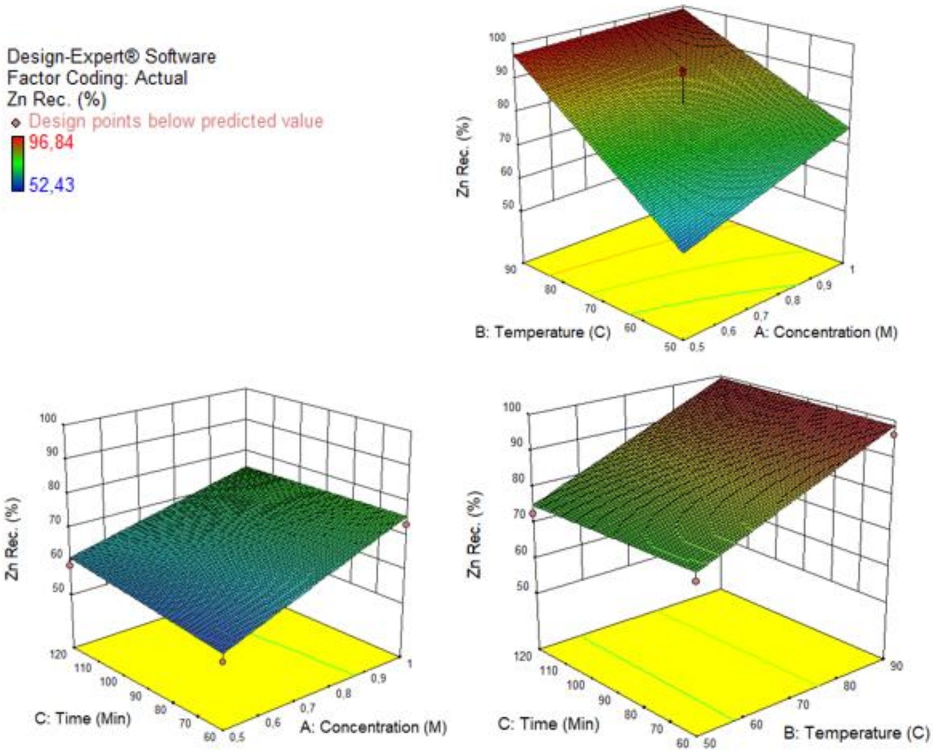


Figure 4.14 3-D Graphical Representation Change in Zinc Extraction Ratio by using Citric Acid with respect to Three Operational Parameters and to Their Combination.

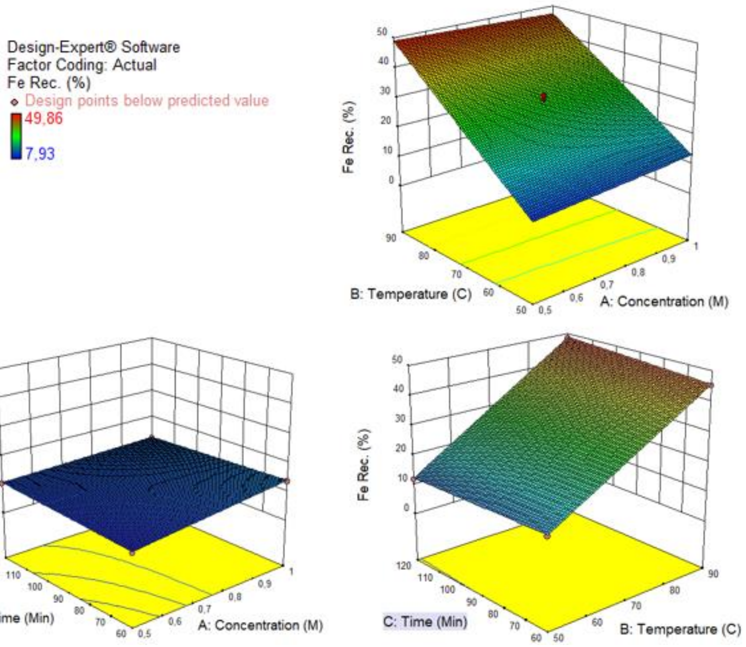


Figure 4.15 3-D Graphical Representation Change in Iron Extraction Ratio by using Citric Acid with respect to Three Operational Parameters and to Their Combination.

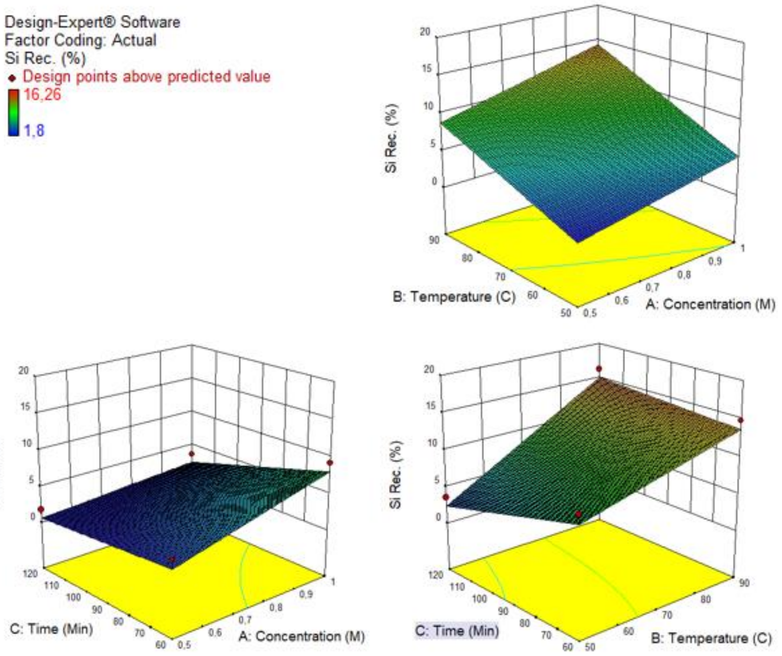


Figure 4.16 3-D Graphical Representation Change in Silica Extraction Ratio by using Citric Acid with respect to Three Operational Parameters and to Their Combination.

Within the consideration of 3-D graphical representation of zinc extraction respect to operational parameters, the most significant operational parameter on zinc extraction is temperature. In addition to that, although not as significant as temperature, citric acid concentration also improve extraction ratio of zinc. As it was inferred during the evaluation of constructed equations, temperature is the most critical parameter for dissolution rate of iron. Decrease in temperature supports rejection of iron. The other operational parameters such as leaching time and citric acid concentration does not change dissolution of iron. Moreover, temperature also directly effects dissolution of silica and in addition, interrelation between leaching time and citric acid concentration has the direct impact on silica dissolution rate. As the result of conducted evaluation by using Design Expert program optimum leaching test using citric acid has been determined by considering maximum zinc extraction ratio and minimum dissolution rates of Fe and Si. Determined optimum operational parameters are 1M citric acid concentration, 50°C temperature and 120 min leaching time yielding 75.09% zinc extraction rate, 12.37% iron dissolution rate and 2.37% silica dissolution rate. Output of the software presenting optimum test condition is given in the Table 4.21.

Table 4.21 Optimum Test Conditions Determined by the Program

Test Conditions			**Extraction Rates**		
Reagent Concentration	**Temperature (C°)**	**Leaching Time (min.)**	**Zn (%)**	**Fe (%)**	**Si (%)**
1M	50	120	75.09	12.37	2.37

4.2.5. Ammonium Carbonate Leaching

Within the scope of ammonium carbonate leaching study, systematic leaching tests were performed in order to evaluate the effects of each variable parameters in terms of selective extraction of zinc by leaving impurities in leach residue. As it was in other leaching tests, main motivation is to maximize zinc extraction ratio and minimize Fe and Si dissolution rates as the major impurities. Range of applied operational parameters are indicated in Table 4.22.

Table 4.22 Range of Operational Parameters Applied for Ammonium Carbonate Leaching

Parameter	**Lower Level**	**Base Level**	**Higher Level**
Acid Concentration	1 M	2 M	3 M
Temperature	30 C°	40 C°	50 C°
Leaching Time	60 min.	120 min.	180 min.

Performance of the ammonium carbonate leaching test were evaluated within the consideration of extraction ratio of zinc and dissolution rates of iron and silica. According to chemical analysis of leach residues metallurgical balance tables were constructed which provide information about leaching performance. Extraction ratio of zinc, dissolution rates of iron and silica with operation parameters of tests are given in the Table 4.23.

Table 4.23 Extraction Ratio of Zinc and Main Impurities with respect to Change in Operational Parameters

Reagent Conc.	**Temp. (C°)**	**Time (hour)**	**Zn Ext. Rat. (%)**	**Fe Ext. Rat. (%)**	**Si Ext. Rat. (%)**
1M	1	50	4.47	9.90	6.57
2M	2	40	2.99	11.24	1.54
1M	3	50	8.58	11.20	**8.97**
2M	2	40	11.25	**14.39**	5.75
3M	3	50	20.94	12.33	4.56
3M	1	30	10.36	**8.70**	2.55
1M	1	30	**2.14**	10.07	**1.25**
3M	1	50	17.99	11.58	1.53
1M	3	30	2.67	10.17	4.42
3M	3	30	**23.06**	14.10	3.75

As it was seen Table 4.23, maximum and minimum extraction ratios of the zinc are obtained as 23.06% and 2.14% respectively which means greatest part of the zinc content remained in the leach residue part as the result of performed leaching process. In addition to that maximum and minimum dissolution rates of the Fe and Si are 14.39% (Fe), 8.70% (Fe) and 8.97% (Si) and 1.25% (Si) respectively which may be greater than extraction ratio of zinc within the scope of several tests. Even the dissolution rate as much as 14.39% would be tolerated in the case of higher extraction ratio of zinc is obtained since zinc extraction ratios are already low, impurity dissolution rates become more and more important. Due to the lower extraction rates of zinc, ammonium carbonate leaching couldn't be found as feasible under these operational conditions. For this reason statistical model was not be constructed.

4.2.6. Boric Acid Leaching

Within the scope of boric leaching study, systematic tests were performed in order to evaluate effects of each variable parameters in terms of selective extraction of zinc by leaving impurities in leach residue. As it was in other leaching tests main motivation is to maximize zinc extraction ratio and minimize Fe and Si dissolution rates as a major impurities. Range of applied operational parameters are indicated in Table 4.24.

Table 4.24 Range of Operational Parameters Applied for Boric Acid Leaching

Parameter	Lower Level	Base Level	Higher Level
Acid Concentration	0.5 M	0.75M	1 M
Temperature	40 C°	60 C°	80 C°
Leaching Time	30 min.	60 min.	90 min.

Performance of the boric acid leaching test were evaluated within the consideration of extraction ratio of zinc and dissolution rates of iron and silica. According to the chemical analysis of leach residues metallurgical balance tables were constructed which provide information about leaching performance. Extraction ratio of zinc, dissolution rates of iron and silica with operation parameters of tests are given in the Table 4.25.

Table 4.25 Extraction Ratio of Zinc and Main Impurities with respect to Change in Operational Parameters

Reagent Conc.	Time (min.)	Temp. (C°)	Zn Ext. Rat. (%)	Fe Ext. Rat. (%)	Si Ext. Rat. (%)
0.5M	30.00	80.00	7.43	**2.30**	14.80
0.75M	60.00	60.00	**3.06**	18.72	12.63
0.5M	90.00	80.00	10.56	5.57	17.26
0.75M	60.00	60.00	8.02	**20.51**	13.21
1M	90.00	80.00	10.02	3.21	16.71

Table 4.26 Extraction Ratio of Zinc and Main Impurities with respect to Change in Operational Parameters (cont'd)

1M	30.00	40.00	9.19	6.26	19.27
0.5M	30.00	40.00	9.02	4.03	17.05
1M	30.00	80.00	11.23	22.37	**8.72**
0.5M	90.00	40.00	12.47	6.77	**18.33**
1M	90.00	40.00	**16.32**	10.71	18.26

As it was seen Table 4.25, maximum and minimum extraction ratios of the zinc are obtained as 16.32% and 3.06% respectively which means greatest part of the zinc content remained in the leach residue part as the result of conducted leaching process. In addition to that maximum and minimum dissolution rates of the Fe and Si are 20.51% (Fe), 2.30% (Fe) and 18.33% (Si) and 8.72% (Si) respectively which may be greater than extraction ratio of zinc within the scope of several tests. Due to lower extraction rates of zinc, boric acid leaching couldn't be found as feasible under these operational conditions. For this reason statistical model was not constructed.

4.2.7. Optimum Leaching Test

With the aim of extraction of zinc from flotation tailing several leaching tests were conducted by using six different chemical under varying operational parameters. Leaching test performed by using ammonium carbonate and boric acid found as unsuccessful in terms of zinc extraction ratios according to metallurgical balance calculations conducted according to chemical analysis result of the leach residues. On the other hand, sulphuric acid leaching, ammonia leaching, ammonium chloride leaching and citric acid leaching test result provide reasonable high zinc extraction ratios. From the technical and economic point of view rejection of impurities and operational parameters were consider as much as zinc extraction ratio. From this point of view ammonium chloride would be determined as the best reagent from the technical point of view since optimum test obtained by statistical model provide 87.81% Zn extraction ratio and 12.69% Fe and 20.63% Si dissolution rates by using 5M ammonium chloride under 90°C temperature leached for 60 minutes. On the other hand, sulphuric acid leaching found as more applicable industrially and from the economical point of view more realistic due to it’s advantageous operational conditions. Optimum test conditions for sulphuric acid leaching according to statistical model provides 96.63% Zn extraction with 35.47% Fe and 8.52% Si dissolution was obtained by using 1M sulphuric acid under 30°C temperature leached for 60 minutes.

Table 4.27 Proposed Leaching Lixiviants and Related Operational Conditions

Lixiviant	**Concentration (M)**	**Temperature (°C)**	**Duration (minute)**	**Zn Ext. (%)**	**Fe Diss. (%)**	**Si Diss. (%)**
NH_4Cl	5	90	60	87.81	12.69	20.63
H_2SO_4	1	30	60	96.63	35.47	8.52

CHAPTER 5

CONCLUSION

Within the scope of this thesis study, ore material obtained from Yozgat region of Turkey was used which contains 3.17% Pb, 6.19% Zn as valuable entity and 6.72% Fe, 23.2% Si as the major impurity elements according to performed chemical analysis results. In addition to that the ore contains 4.35% Al, 0.61% Ca and 0.52% Mg as the minor impurity elements. Mineralogical composition of the ore was determined by using optical microscope and X-Ray Diffractometer. Based on the minerological and petrographical analysis, ore materials has been intensely weathered and oxidized and are characterized by predominant silica-clay carbonate-oxide assemblages. It was determined that lead carbonate mineral ($PbCO_3$) and zinc carbonate mineral ($ZnCO_3$) contained within the ore sample which were likely formed due to whethering of their sulphide counterparts. In addition to that, quartz and goethite would be classified as the major gangue minerals. Within the context of the separation of valuable minerals from each other and gangue entities two methods namely flotation and leaching was applied. In order to obtain cerussite concentrate by conventional flotation concentration method by using 250 g/t Na_2SiO_3 as dispersant (conditioned for 10 minutes), H_2SO_4 as pH regulator, 4000 g/t Na_2S as sulfidizer agent (conditioned for 15 minutes), 500 g/t PAX as collector (conditioned for 10 minutes) and 75 g/t F-533 as frother was applied. In order to obtain maximum possible grade at a reasonable recovery values 3 cleaning stages without additional reagent utilization was conducted. As the result of flotation tests cerussite concentrate with 60.20% Pb grade at 64.29% recovery was obtained. With the motivation to obtain zinc from cerussite flotation tailings, six different leaching reagent was used namely sulphuric acid, ammonia, ammonium chloride, ammonium carbonate, citric acid and boric acid. According to the chemical analysis, results of boric acid leaching and ammonium carbonate leaching was found as unsuccessful since Zn extraction ratios were calculated as low as experiments would not be classified as technically and economically feasible. However as a result of sulfuric acid leaching, citric acid leaching, ammonia leaching and ammonium chloride leaching, high Zn extraction ratio at acceptable technical and economical frame were obtained. From the technical and economical point of view rejection of impurities, temperature and chemical consumption were considered as much as zinc extraction rate. In accordance with these criteria, ammonium chloride would be determined as the best reagent from the technical point of view since optimum test determined by statistical model provide 87.81% Zn extraction ratio and 12.69% Fe and 20.63% Si dissolution rates by using 5M ammonium chloride under 90°C temperature leached for 60 minutes. Contrary to this, within the consideration of industrial applicability, sulphuric acid leaching would be evaluated as a reasonable option. Operational and economic applicability of sulphuric acid found as more realistic since determined optimum test conditions by using statistical model, 96.63% Zn extraction with 35.47% Fe and 8.52% Si dissolution was obtained by using 1M sulphuric acid under 30°C temperature leached for 60 minutes.

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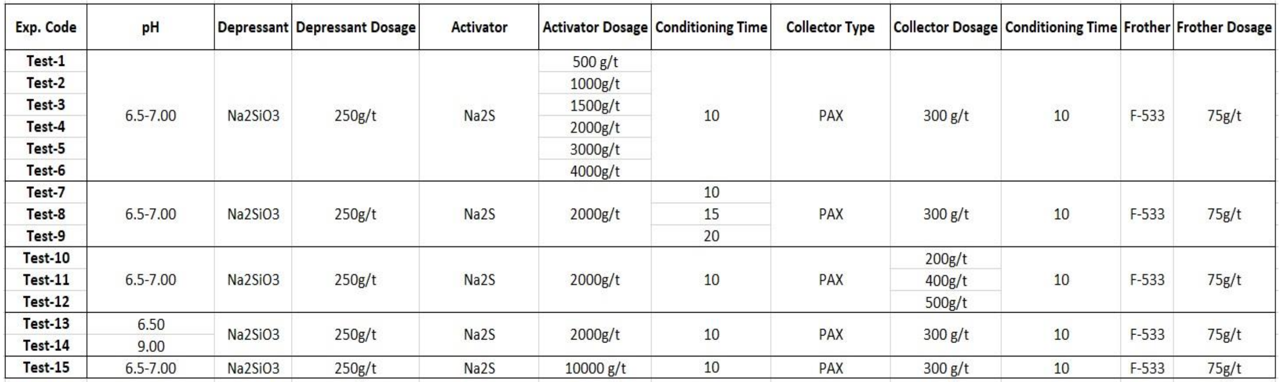
APPENDICES

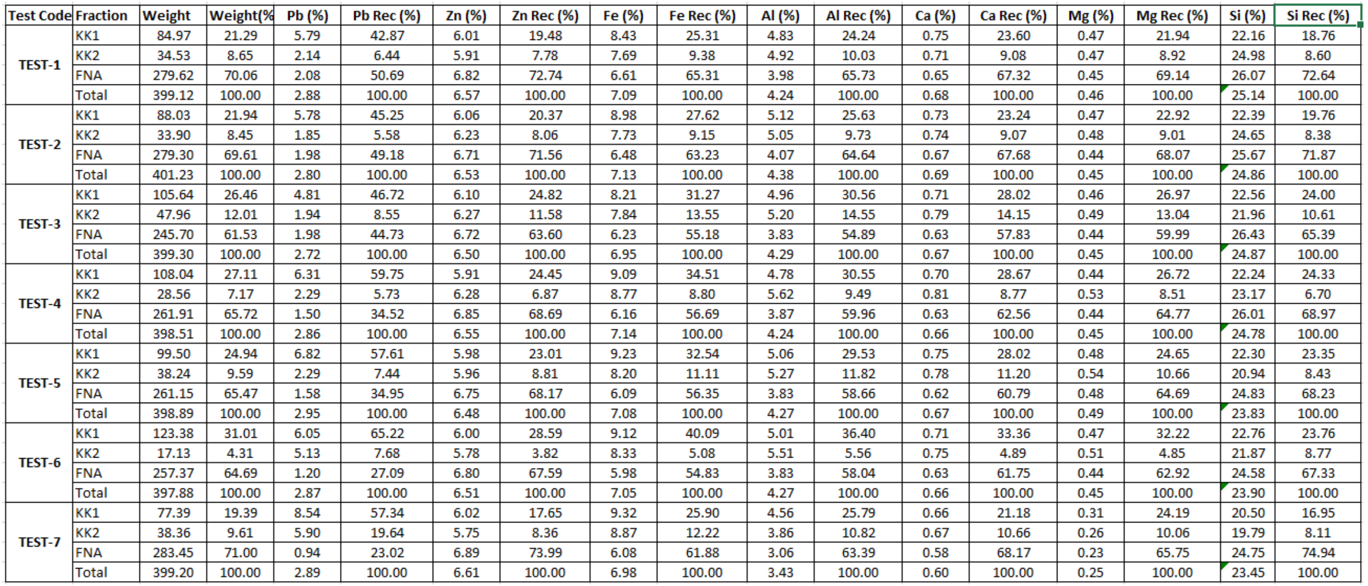
A. Flotation Tests

Table A. 1 Operational Conditions of Conducted Flotation Tests



Exp. Code	pH	Depressant	Depressant Dosage	Activator	Activator Dosage	Conditioning Time	Collector Type	Collector Dosage	Conditioning Time	Frother	Frother Dosage
Test-1	6.5-7.00	Na2SiO3	250g/t	Na2S	500 g/t	10	PAX	300 g/t	10	F-533	75g/t
Test-2					1000g/t						
Test-3					1500g/t						
Test-4					2000g/t						
Test-5					3000g/t						
Test-6					4000g/t						
Test-7	6.5-7.00	Na2SiO3	250g/t	Na2S	2000g/t	10	PAX	300 g/t	10	F-533	75g/t
Test-8						15					
Test-9						20					
Test-10	6.5-7.00	Na2SiO3	250g/t	Na2S	2000g/t	10	PAX	200g/t	10	F-533	75g/t
Test-11								400g/t			
Test-12								500g/t			
Test-13	6.50	Na2SiO3	250g/t	Na2S	2000g/t	10	PAX	300 g/t	10	F-533	75g/t
Test-14	9.00										
Test-15	6.5-7.00	Na2SiO3	250g/t	Na2S	10000 g/t	10	PAX	300 g/t	10	F-533	75g/t

Table A. 2 Effect of Change in Activator Dosage on Grade and Recovery Values of Elements



Test Code	Fraction	Weight	Weight(%	Pb (%)	Pb Rec (%)	Zn (%)	Zn Rec (%)	Fe (%)	Fe Rec (%)	Al (%)	Al Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
TEST-1	KK1	84.97	21.29	5.79	42.87	6.01	19.48	8.43	25.31	4.83	24.24	0.75	23.60	0.47	21.94	22.16	18.76
	KK2	34.53	8.65	2.14	6.44	5.91	7.78	7.69	9.38	4.92	10.03	0.71	9.08	0.47	8.92	24.98	8.60
	FNA	279.62	70.06	2.08	50.69	6.82	72.74	6.61	65.31	3.98	65.73	0.65	67.32	0.45	69.14	26.07	72.64
	Total	399.12	100.00	2.88	100.00	6.57	100.00	7.09	100.00	4.24	100.00	0.68	100.00	0.46	100.00	25.14	100.00
TEST-2	KK1	88.03	21.94	5.78	45.25	6.06	20.37	8.98	27.62	5.12	25.63	0.73	23.24	0.47	22.92	22.39	19.76
	KK2	33.90	8.45	1.85	5.58	6.23	8.06	7.73	9.15	5.05	9.73	0.74	9.07	0.48	9.01	24.65	8.38
	FNA	279.30	69.61	1.98	49.18	6.71	71.56	6.48	63.23	4.07	64.64	0.67	67.68	0.44	68.07	25.67	71.87
	Total	401.23	100.00	2.80	100.00	6.53	100.00	7.13	100.00	4.38	100.00	0.69	100.00	0.45	100.00	24.86	100.00
TEST-3	KK1	105.64	26.46	4.81	46.72	6.10	24.82	8.21	31.27	4.96	30.56	0.71	28.02	0.46	26.97	22.56	24.00
	KK2	47.96	12.01	1.94	8.55	6.27	11.58	7.84	13.55	5.20	14.55	0.79	14.15	0.49	13.04	21.96	10.61
	FNA	245.70	61.53	1.98	44.73	6.72	63.60	6.23	55.18	3.83	54.89	0.63	57.83	0.44	59.99	26.43	65.39
	Total	399.30	100.00	2.72	100.00	6.50	100.00	6.95	100.00	4.29	100.00	0.67	100.00	0.45	100.00	24.87	100.00
TEST-4	KK1	108.04	27.11	6.31	59.75	5.91	24.45	9.09	34.51	4.78	30.55	0.70	28.67	0.44	26.72	22.24	24.33
	KK2	28.56	7.17	2.29	5.73	6.28	6.87	8.77	8.80	5.62	9.49	0.81	8.77	0.53	8.51	23.17	6.70
	FNA	261.91	65.72	1.50	34.52	6.85	68.69	6.16	56.69	3.87	59.96	0.63	62.56	0.44	64.77	26.01	68.97
	Total	398.51	100.00	2.86	100.00	6.55	100.00	7.14	100.00	4.24	100.00	0.66	100.00	0.45	100.00	24.78	100.00
TEST-5	KK1	99.50	24.94	6.82	57.61	5.98	23.01	9.23	32.54	5.06	29.53	0.75	28.02	0.48	24.65	22.30	23.35
	KK2	38.24	9.59	2.29	7.44	5.96	8.81	8.20	11.11	5.27	11.82	0.78	11.20	0.54	10.66	20.94	8.43
	FNA	261.15	65.47	1.58	34.95	6.75	68.17	6.09	56.35	3.83	58.66	0.62	60.79	0.48	64.69	24.83	68.23
	Total	398.89	100.00	2.95	100.00	6.48	100.00	7.08	100.00	4.27	100.00	0.67	100.00	0.49	100.00	23.83	100.00
TEST-6	KK1	123.38	31.01	6.05	65.22	6.00	28.59	9.12	40.09	5.01	36.40	0.71	33.36	0.47	32.22	22.76	23.76
	KK2	17.13	4.31	5.13	7.68	5.78	3.82	8.33	5.08	5.51	5.56	0.75	4.89	0.51	4.85	21.87	8.77
	FNA	257.37	64.69	1.20	27.09	6.80	67.59	5.98	54.83	3.83	58.04	0.63	61.75	0.44	62.92	24.58	67.33
	Total	397.88	100.00	2.87	100.00	6.51	100.00	7.05	100.00	4.27	100.00	0.66	100.00	0.45	100.00	23.90	100.00
TEST-7	KK1	77.39	19.39	8.54	57.34	6.02	17.65	9.32	25.90	4.56	25.79	0.66	21.18	0.31	24.19	20.50	16.95
	KK2	38.36	9.61	5.90	19.64	5.75	8.36	8.87	12.22	3.86	10.82	0.67	10.66	0.26	10.06	19.79	8.11
	FNA	283.45	71.00	0.94	23.02	6.89	73.99	6.08	61.88	3.06	63.39	0.58	68.17	0.23	65.75	24.75	74.94
	Total	399.20	100.00	2.89	100.00	6.61	100.00	6.98	100.00	3.43	100.00	0.60	100.00	0.25	100.00	23.45	100.00

Table A. 3 Effect of Change in Activator Conditioning Time on Grade and Recovery Values of Elements

Test Code	Fraction	Weight	Weight/%	Pb (%)	Pb Rec (%)	Zn (%)	Zn Rec (%)	Fe (%)	Fe Rec(%)	Al (%)	Al Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
Test-8	KK1	99.87	25.04	6.76	58.79	5.93	23.37	8.89	32.35	4.95	29.37	0.76	28.38	0.50	25.82	22.47	25.10
	KK2	32.48	8.14	2.03	5.74	5.78	7.41	8.09	9.57	5.50	10.61	0.81	9.84	0.56	9.40	20.57	7.47
	FNA	266.57	66.82	1.53	35.47	6.58	69.22	5.98	58.08	3.79	60.02	0.62	61.79	0.47	64.78	22.62	67.43
	Total	398.92	100.00	2.88	100.00	6.35	100.00	6.88	100.00	4.22	100.00	0.67	100.00	0.48	100.00	22.42	100.00
Test-9	KK1	136.76	34.33	5.40	63.25	6.05	31.98	8.54	41.93	4.86	39.30	0.75	37.18	0.51	35.36	21.21	30.16
	KK2	32.22	8.09	2.15	5.93	6.42	7.99	7.62	8.81	5.01	9.55	0.75	8.76	0.54	8.82	23.27	7.80
	FNA	229.43	57.59	1.57	30.81	6.77	60.03	5.98	49.26	3.77	51.15	0.65	54.06	0.48	55.82	26.01	62.05
	Total	398.41	100.00	2.93	100.00	6.49	100.00	6.99	100.00	4.24	100.00	0.69	100.00	0.50	100.00	24.14	100.00
Test-10	KK1	119.70	30.06	5.03	52.52	5.96	27.55	8.69	37.53	4.91	34.06	0.73	32.72	0.50	30.26	22.02	27.17
	KK2	21.15	5.31	2.24	4.14	6.20	5.06	8.01	6.11	5.51	6.75	0.83	6.57	0.56	5.99	21.30	4.64
	FNA	257.31	64.62	1.93	43.34	6.78	67.38	6.07	56.36	3.97	59.19	0.63	60.70	0.49	63.75	25.71	68.19
	Total	398.16	100.00	2.88	100.00	6.50	100.00	6.96	100.00	4.33	100.00	0.67	100.00	0.50	100.00	24.37	100.00

Table A. 4 Effect of Change in Collector Dosage on Grade and Recovery Values of Elements

Test Code	Fraction	Weight	Weight/%	Pb (%)	Pb Rec (%)	Zn (%)	Zn Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
Test-11	KK1	113.72	28.49	5.08	51.49	6.15	26.41	0.69	30.72	0.50	29.17	23.33	26.07
	KK2	22.10	5.54	2.12	4.17	6.09	5.08	0.74	6.40	0.53	6.01	20.58	4.47
	FNA	263.30	65.97	1.89	44.33	6.89	68.51	0.61	62.88	0.48	64.83	26.84	69.46
	Total	399.12	100.00	2.81	100.00	6.63	100.00	0.64	100.00	0.49	100.00	25.49	100.00
Test-12	KK1	120.09	30.11	5.35	58.50	6.16	28.63	0.75	34.36	0.54	32.94	22.69	28.17
	KK2	34.13	8.56	1.99	6.19	6.13	8.10	0.74	9.63	0.57	9.88	25.51	9.00
	FNA	244.68	61.34	1.58	35.31	6.68	63.27	0.60	56.01	0.46	57.18	24.84	62.83
	Total	398.90	100.00	2.75	100.00	6.48	100.00	0.66	100.00	0.49	100.00	24.25	100.00
Test-13	KK1	111.70	28.00	6.45	61.35	5.82	25.09	0.76	31.23	0.48	13.23	22.90	27.32
	KK2	25.55	6.40	2.10	4.57	5.90	5.82	0.76	7.14	0.58	3.66	20.66	5.64
	FNA	261.74	65.60	1.53	34.08	6.84	69.09	0.64	61.63	0.49	31.65	23.98	67.04
	Total	398.99	100.00	2.95	100.00	6.49	100.00	0.68	100.00	1.02	100.00	23.47	100.00

Table A. 5 Effect of Change in Pulp pH on Grade and Recovery Values of Elements

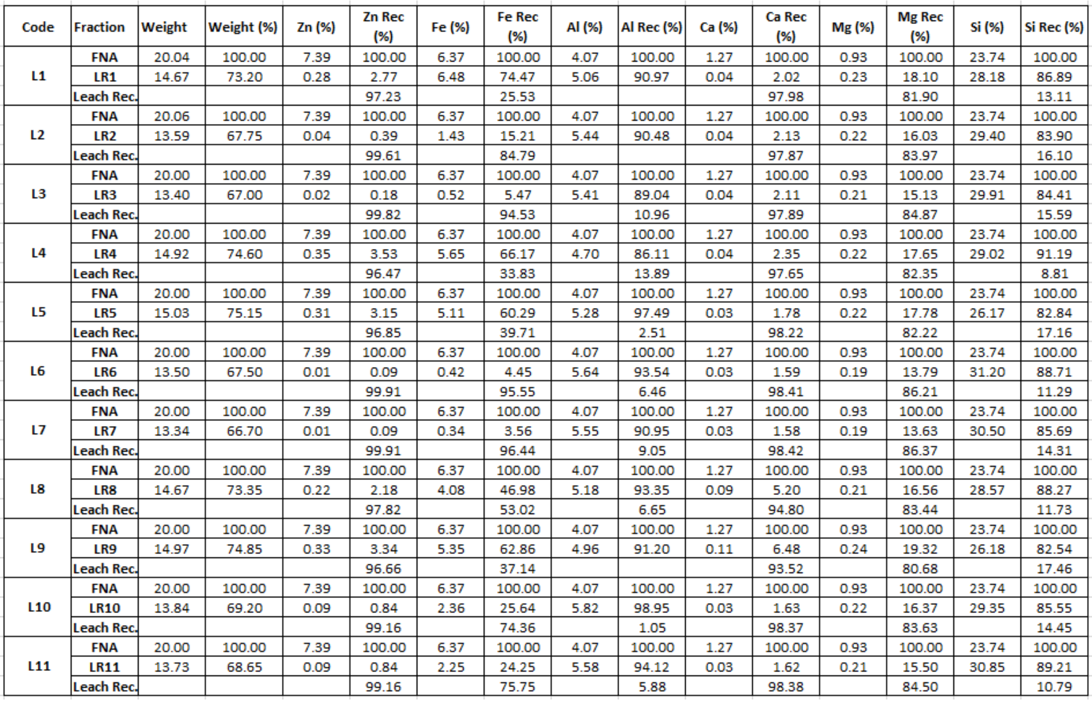
Test Code	Fraction	Weight	Weight/%	Pb (%)	Pb Rec (%)	Zn (%)	Zn Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
Test-14	KK1	125.15	31.83	5.71	62.75	5.99	28.48	0.69	33.97	0.52	32.72	22.90	31.03
	KK2	17.97	4.57	2.64	4.17	5.69	3.88	0.71	5.02	0.35	3.16	20.66	4.02
	FNA	250.10	63.60	1.51	33.08	7.12	67.64	0.62	61.01	0.51	64.12	23.98	64.94
	Total	393.22	100.00	2.89	100.00	6.70	100.00	0.65	100.00	0.51	100.00	23.48	100.00
Test-15	KK1	128.39	32.44	3.25	40.78	5.94	29.64	0.50	29.28	0.26	28.60	21.50	34.00
	KK2	17.03	4.30	5.88	9.79	5.45	3.61	0.43	3.34	0.19	2.77	18.62	3.91
	FNA	250.34	63.26	2.02	49.43	6.86	66.75	0.59	67.38	0.32	68.63	20.14	62.10
	Total	395.76	100.00	2.59	100.00	6.50	100.00	0.55	100.00	0.29	100.00	20.52	100.00

Table A. 6 Metallurgical Balance Table Related with Optimum Flotation Test

Fraction	Weight	Weight (%)	Pb (%)	Pb Rec (%)	Zn (%)	Zn Rec (%)	Fe (%)	Fe Rec (%)	Al (%)	Al Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
Lead Concentrate	12.50	3.14	60.20	64.29	1.90	0.91	3.25	1.49	2.25	1.65	0.45	2.17	0.51	4.03	5.76	0.76
Cleaner Tailing-3	15.05	3.78	4.50	5.79	4.70	2.72	7.60	4.18	3.21	2.84	0.54	3.13	0.45	4.28	12.05	1.92
Cleaner Tailing-2	25.06	6.29	1.02	2.18	4.96	4.78	8.50	7.79	4.55	6.70	0.45	4.35	0.66	10.45	15.06	3.99
Cleaner Tailing-1	85.28	21.40	0.60	4.37	6.40	20.98	10.12	31.56	5.75	28.81	0.55	18.07	0.56	30.19	27.05	24.39
Final Tailing	260.54	65.39	1.05	23.37	7.05	70.61	5.77	54.98	3.92	60.00	0.72	72.28	0.31	51.05	25.02	68.94
Total	398.43	100.00	2.94	100.00	6.53	100.00	6.86	100.00	4.27	100.00	0.65	15.25	0.40	100.00	23.73	100.00

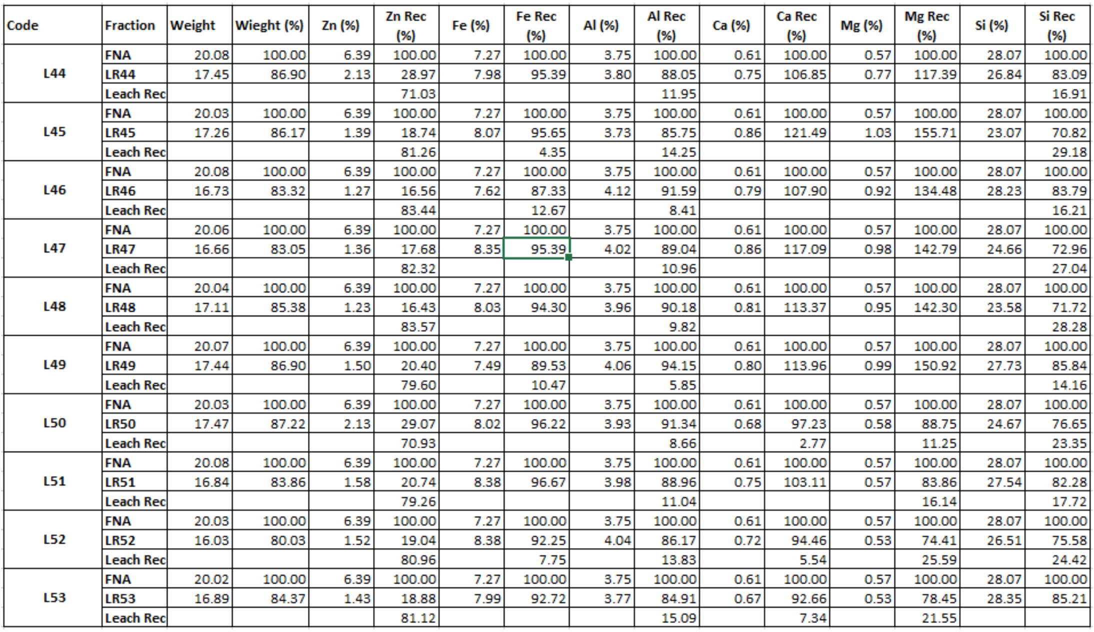
B. Leaching Tests

Table B. 1 Metallurgical Balance Table of Sulphuric Acid Leaching Tests



Code	Fraction	Weight	Weight (%)	Zn (%)	Zn Rec (%)	Fe (%)	Fe Rec (%)	Al (%)	Al Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
L1	**FNA**	20.04	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR1	14.67	73.20	0.28	2.77	6.48	74.47	5.06	90.97	0.04	2.02	0.23	18.10	28.18	86.89
	Leach Rec.				97.23		25.53				97.98		81.90		13.11
L2	**FNA**	20.06	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR2	13.59	67.75	0.04	0.39	1.43	15.21	5.44	90.48	0.04	2.13	0.22	16.03	29.40	83.90
	Leach Rec.				99.61		84.79				97.87		83.97		16.10
L3	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR3	13.40	67.00	0.02	0.18	0.52	5.47	5.41	89.04	0.04	2.11	0.21	15.13	29.91	84.41
	Leach Rec.				99.82		94.53		10.96		97.89		84.87		15.59
L4	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR4	14.92	74.60	0.35	3.53	5.65	66.17	4.70	86.11	0.04	2.35	0.22	17.65	29.02	91.19
	Leach Rec.				96.47		33.83		13.89		97.65		82.35		8.81
L5	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR5	15.03	75.15	0.31	3.15	5.11	60.29	5.28	97.49	0.03	1.78	0.22	17.78	26.17	82.84
	Leach Rec.				96.85		39.71		2.51		98.22		82.22		17.16
L6	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR6	13.50	67.50	0.01	0.09	0.42	4.45	5.64	93.54	0.03	1.59	0.19	13.79	31.20	88.71
	Leach Rec.				99.91		95.55		6.46		98.41		86.21		11.29
L7	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR7	13.34	66.70	0.01	0.09	0.34	3.56	5.55	90.95	0.03	1.58	0.19	13.63	30.50	85.69
	Leach Rec.				99.91		96.44		9.05		98.42		86.37		14.31
L8	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR8	14.67	73.35	0.22	2.18	4.08	46.98	5.18	93.35	0.09	5.20	0.21	16.56	28.57	88.27
	Leach Rec.				97.82		53.02		6.65		94.80		83.44		11.73
L9	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR9	14.97	74.85	0.33	3.34	5.35	62.86	4.96	91.20	0.11	6.48	0.24	19.32	26.18	82.54
	Leach Rec.				96.66		37.14				93.52		80.68		17.46
L10	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR10	13.84	69.20	0.09	0.84	2.36	25.64	5.82	98.95	0.03	1.63	0.22	16.37	29.35	85.55
	Leach Rec.				99.16		74.36		1.05		98.37		83.63		14.45
L11	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR11	13.73	68.65	0.09	0.84	2.25	24.25	5.58	94.12	0.03	1.62	0.21	15.50	30.85	89.21
	Leach Rec.				99.16		75.75		5.88		98.38		84.50		10.79

Table B. 2 Metallurgical Balance Table of Ammonia Leaching Tests

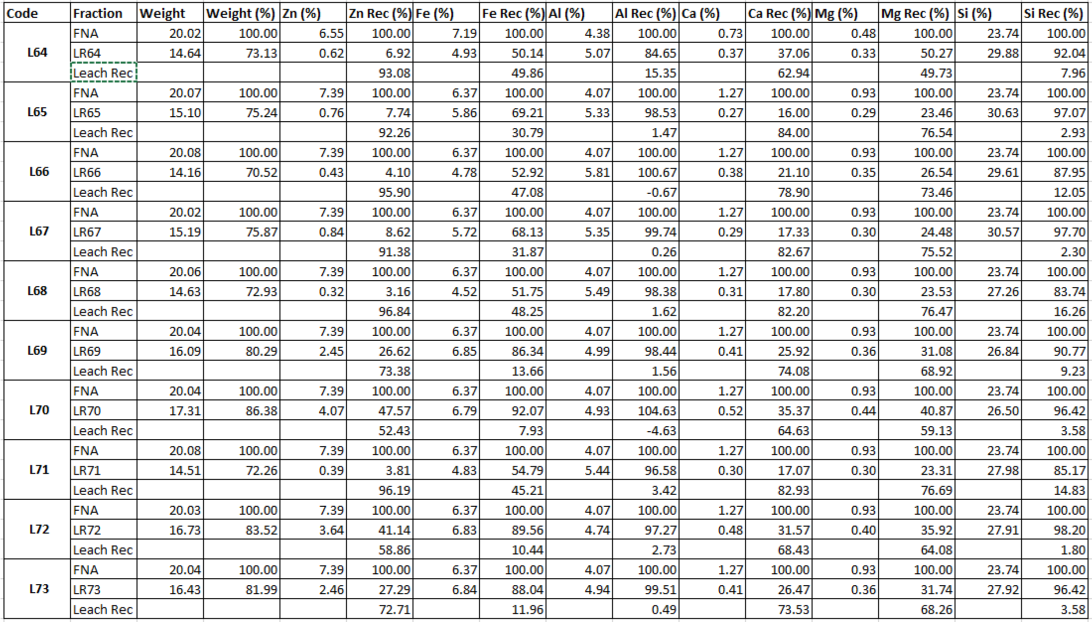


Code	Fraction	Weight	Wieght (%)	Zn (%)	Zn Rec (%)	Fe (%)	Fe Rec (%)	Al (%)	Al Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
L44	**FNA**	20.08	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR44	17.45	86.90	2.13	28.97	7.98	95.39	3.80	88.05	0.75	106.85	0.77	117.39	26.84	83.09
	Leach Rec				71.03				11.95						16.91
L45	**FNA**	20.03	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR45	17.26	86.17	1.39	18.74	8.07	95.65	3.73	85.75	0.86	121.49	1.03	155.71	23.07	70.82
	Leach Rec				81.26		4.35		14.25						29.18
L46	**FNA**	20.08	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR46	16.73	83.32	1.27	16.56	7.62	87.33	4.12	91.59	0.79	107.90	0.92	134.48	28.23	83.79
	Leach Rec				83.44		12.67		8.41						16.21
L47	**FNA**	20.06	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR47	16.66	83.05	1.36	17.68	8.35	95.39	4.02	89.04	0.86	117.09	0.98	142.79	24.66	72.96
	Leach Rec				82.32				10.96						27.04
L48	**FNA**	20.04	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR48	17.11	85.38	1.23	16.43	8.03	94.30	3.96	90.18	0.81	113.37	0.95	142.30	23.58	71.72
	Leach Rec				83.57				9.82						28.28
L49	**FNA**	20.07	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR49	17.44	86.90	1.50	20.40	7.49	89.53	4.06	94.15	0.80	113.96	0.99	150.92	27.73	85.84
	Leach Rec				79.60		10.47		5.85						14.16
L50	**FNA**	20.03	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR50	17.47	87.22	2.13	29.07	8.02	96.22	3.93	91.34	0.68	97.23	0.58	88.75	24.67	76.65
	Leach Rec				70.93				8.66		2.77		11.25		23.35
L51	**FNA**	20.08	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR51	16.84	83.86	1.58	20.74	8.38	96.67	3.98	88.96	0.75	103.11	0.57	83.86	27.54	82.28
	Leach Rec				79.26				11.04				16.14		17.72
L52	**FNA**	20.03	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR52	16.03	80.03	1.52	19.04	8.38	92.25	4.04	86.17	0.72	94.46	0.53	74.41	26.51	75.58
	Leach Rec				80.96		7.75		13.83		5.54		25.59		24.42
L53	**FNA**	20.02	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR53	16.89	84.37	1.43	18.88	7.99	92.72	3.77	84.91	0.67	92.66	0.53	78.45	28.35	85.21
	Leach Rec				81.12				15.09		7.34		21.55		

Table B. 3 Metallurgical Balance Table of Ammonium Chloride Leaching Tests

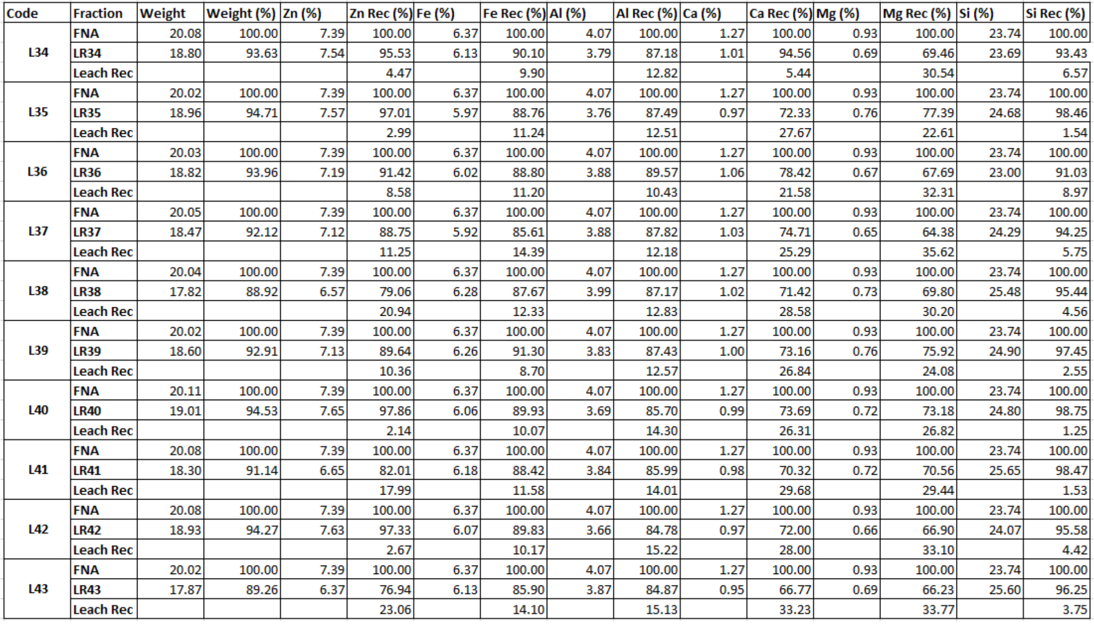
Code	Fraction	Weight	Weight (%)	Zn (%)	Zn Rec (%)	Fe (%)	Fe Rec (%)	Al (%)	Al Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
L23	**FNA**	20.02	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR23	15.48	77.32	1.19	12.45	7.21	87.52	5.07	96.30	0.73	44.45	0.62	51.55	28.00	91.20
	Leach Rec.				87.55		12.48		3.70		55.55		48.45		8.80
L24	**FNA**	20.07	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR24	17.20	85.70	4.56	52.88	6.49	87.31	4.52	95.24	0.84	56.68	0.69	63.58	23.86	86.13
	Leach Rec.				47.12		12.69		4.76		43.32		36.42		13.87
L25	**FNA**	20.00	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR25	15.40	77.00	1.17	12.19	7.56	91.38	5.17	97.89	0.35	21.22	0.39	32.29	25.52	82.77
	Leach Rec.				87.81		8.62		2.11		78.78		67.71		17.23
L27	**FNA**	20.05	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR27	17.14	85.49	4.92	56.91	6.64	89.11	4.59	96.48	0.87	58.56	0.71	65.26	23.60	84.98
	Leach Rec.				43.09		10.89		3.52		41.44		34.74		15.02
L28	**FNA**	20.12	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR28	15.83	78.68	1.41	15.01	7.41	91.52	4.99	96.45	0.75	46.46	0.62	52.45	25.50	84.51
	Leach Rec.				84.99		8.48		3.55		53.54		47.55		15.49
L29	**FNA**	20.03	100.00	7.39		6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR29	18.73	93.51	8.36	105.78	6.14	90.13	4.16	95.63	0.84	61.85	0.69	69.38	22.46	88.47
	Leach Rec.						9.87		4.37		38.15		30.62		11.53
L30	**FNA**	20.03	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR30	17.25	86.12	5.97	69.57	6.65	89.91	4.50	95.15	0.89	60.35	0.72	66.67	23.05	83.62
	Leach Rec.				30.43		10.09		4.85		39.65		33.33		16.38
L31	**FNA**	20.03	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR31	16.44	82.08	2.85	31.65	7.09	91.35	4.87	98.14	0.89	57.52	0.73	64.43	25.16	86.99
	Leach Rec.				68.35		8.65		1.86		42.48		35.57		13.01
L32	**FNA**	20.02	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR32	18.17	90.76	7.94	97.51	6.44	91.76	4.34	96.74	0.88	62.89	0.72	70.27	20.76	79.37
	Leach Rec.				2.49		8.24		3.26		37.11		29.73		20.63
L33	**FNA**	20.07	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR33	18.06	89.99	7.86	95.71	6.39	90.27	4.36	96.31	0.88	62.35	0.72	69.67	21.28	80.66
	Leach Rec.				4.29		9.73		3.69		37.65		30.33		19.34

Table B. 4 Metallurgical Balance Table of Citric Acid Leaching Tests



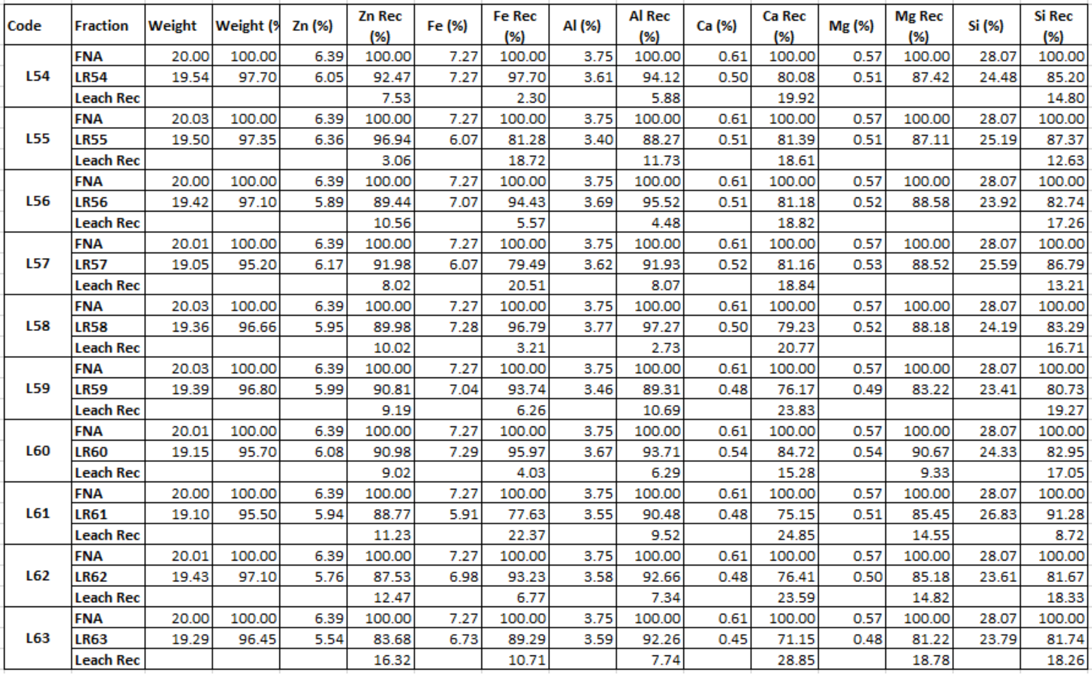
Code	Fraction	Weight	Weight (%)	Zn (%)	Zn Rec (%)	Fe (%)	Fe Rec (%)	Al (%)	Al Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
L64	FNA	20.02	100.00	6.55	100.00	7.19	100.00	4.38	100.00	0.73	100.00	0.48	100.00	23.74	100.00
	LR64	14.64	73.13	0.62	6.92	4.93	50.14	5.07	84.65	0.37	37.06	0.33	50.27	29.88	92.04
	Leach Rec				93.08		49.86		15.35		62.94		49.73		7.96
L65	FNA	20.07	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR65	15.10	75.24	0.76	7.74	5.86	69.21	5.33	98.53	0.27	16.00	0.29	23.46	30.63	97.07
	Leach Rec				92.26		30.79		1.47		84.00		76.54		2.93
L66	FNA	20.08	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR66	14.16	70.52	0.43	4.10	4.78	52.92	5.81	100.67	0.38	21.10	0.35	26.54	29.61	87.95
	Leach Rec				95.90		47.08		-0.67		78.90		73.46		12.05
L67	FNA	20.02	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR67	15.19	75.87	0.84	8.62	5.72	68.13	5.35	99.74	0.29	17.33	0.30	24.48	30.57	97.70
	Leach Rec				91.38		31.87		0.26		82.67		75.52		2.30
L68	FNA	20.06	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR68	14.63	72.93	0.32	3.16	4.52	51.75	5.49	98.38	0.31	17.80	0.30	23.53	27.26	83.74
	Leach Rec				96.84		48.25		1.62		82.20		76.47		16.26
L69	FNA	20.04	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR69	16.09	80.29	2.45	26.62	6.85	86.34	4.99	98.44	0.41	25.92	0.36	31.08	26.84	90.77
	Leach Rec				73.38		13.66		1.56		74.08		68.92		9.23
L70	FNA	20.04	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR70	17.31	86.38	4.07	47.57	6.79	92.07	4.93	104.63	0.52	35.37	0.44	40.87	26.50	96.42
	Leach Rec				52.43		7.93		-4.63		64.63		59.13		3.58
L71	FNA	20.08	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR71	14.51	72.26	0.39	3.81	4.83	54.79	5.44	96.58	0.30	17.07	0.30	23.31	27.98	85.17
	Leach Rec				96.19		45.21		3.42		82.93		76.69		14.83
L72	FNA	20.03	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR72	16.73	83.52	3.64	41.14	6.83	89.56	4.74	97.27	0.48	31.57	0.40	35.92	27.91	98.20
	Leach Rec				58.86		10.44		2.73		68.43		64.08		1.80
L73	FNA	20.04	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR73	16.43	81.99	2.46	27.29	6.84	88.04	4.94	99.51	0.41	26.47	0.36	31.74	27.92	96.42
	Leach Rec				72.71		11.96		0.49		73.53		68.26		3.58

Table B. 5 Metallurgical Balance Table of Ammonium Carbonate Leaching Tests



Code	Fraction	Weight	Weight (%)	Zn (%)	Zn Rec (%)	Fe (%)	Fe Rec (%)	Al (%)	Al Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
L34	**FNA**	20.08	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR34	18.80	93.63	7.54	95.53	6.13	90.10	3.79	87.18	1.01	94.56	0.69	69.46	23.69	93.43
	Leach Rec				4.47		9.90		12.82		5.44		30.54		6.57
L35	**FNA**	20.02	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR35	18.96	94.71	7.57	97.01	5.97	88.76	3.76	87.49	0.97	72.33	0.76	77.39	24.68	98.46
	Leach Rec				2.99		11.24		12.51		27.67		22.61		1.54
L36	**FNA**	20.03	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR36	18.82	93.96	7.19	91.42	6.02	88.80	3.88	89.57	1.06	78.42	0.67	67.69	23.00	91.03
	Leach Rec				8.58		11.20		10.43		21.58		32.31		8.97
L37	**FNA**	20.05	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR37	18.47	92.12	7.12	88.75	5.92	85.61	3.88	87.82	1.03	74.71	0.65	64.38	24.29	94.25
	Leach Rec				11.25		14.39		12.18		25.29		35.62		5.75
L38	**FNA**	20.04	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR38	17.82	88.92	6.57	79.06	6.28	87.67	3.99	87.17	1.02	71.42	0.73	69.80	25.48	95.44
	Leach Rec				20.94		12.33		12.83		28.58		30.20		4.56
L39	**FNA**	20.02	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR39	18.60	92.91	7.13	89.64	6.26	91.30	3.83	87.43	1.00	73.16	0.76	75.92	24.90	97.45
	Leach Rec				10.36		8.70		12.57		26.84		24.08		2.55
L40	**FNA**	20.11	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR40	19.01	94.53	7.65	97.86	6.06	89.93	3.69	85.70	0.99	73.69	0.72	73.18	24.80	98.75
	Leach Rec				2.14		10.07		14.30		26.31		26.82		1.25
L41	**FNA**	20.08	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR41	18.30	91.14	6.65	82.01	6.18	88.42	3.84	85.99	0.98	70.32	0.72	70.56	25.65	98.47
	Leach Rec				17.99		11.58		14.01		29.68		29.44		1.53
L42	**FNA**	20.08	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR42	18.93	94.27	7.63	97.33	6.07	89.83	3.66	84.78	0.97	72.00	0.66	66.90	24.07	95.58
	Leach Rec				2.67		10.17		15.22		28.00		33.10		4.42
L43	**FNA**	20.02	100.00	7.39	100.00	6.37	100.00	4.07	100.00	1.27	100.00	0.93	100.00	23.74	100.00
	LR43	17.87	89.26	6.37	76.94	6.13	85.90	3.87	84.87	0.95	66.77	0.69	66.23	25.60	96.25
	Leach Rec				23.06		14.10		15.13		33.23		33.77		3.75

Table B. 6 Metallurgical Balance Table of Boric Acid Leaching Tests



Code	Fraction	Weight	Weight (9	Zn (%)	Zn Rec (%)	Fe (%)	Fe Rec (%)	Al (%)	Al Rec (%)	Ca (%)	Ca Rec (%)	Mg (%)	Mg Rec (%)	Si (%)	Si Rec (%)
L54	FNA	20.00	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR54	19.54	97.70	6.05	92.47	7.27	97.70	3.61	94.12	0.50	80.08	0.51	87.42	24.48	85.20
	Leach Rec				7.53		2.30		5.88		19.92				14.80
L55	FNA	20.03	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR55	19.50	97.35	6.36	96.94	6.07	81.28	3.40	88.27	0.51	81.39	0.51	87.11	25.19	87.37
	Leach Rec				3.06		18.72		11.73		18.61				12.63
L56	FNA	20.00	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR56	19.42	97.10	5.89	89.44	7.07	94.43	3.69	95.52	0.51	81.18	0.52	88.58	23.92	82.74
	Leach Rec				10.56		5.57		4.48		18.82				17.26
L57	FNA	20.01	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR57	19.05	95.20	6.17	91.98	6.07	79.49	3.62	91.93	0.52	81.16	0.53	88.52	25.59	86.79
	Leach Rec				8.02		20.51		8.07		18.84				13.21
L58	FNA	20.03	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR58	19.36	96.66	5.95	89.98	7.28	96.79	3.77	97.27	0.50	79.23	0.52	88.18	24.19	83.29
	Leach Rec				10.02		3.21		2.73		20.77				16.71
L59	FNA	20.03	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR59	19.39	96.80	5.99	90.81	7.04	93.74	3.46	89.31	0.48	76.17	0.49	83.22	23.41	80.73
	Leach Rec				9.19		6.26		10.69		23.83				19.27
L60	FNA	20.01	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR60	19.15	95.70	6.08	90.98	7.29	95.97	3.67	93.71	0.54	84.72	0.54	90.67	24.33	82.95
	Leach Rec				9.02		4.03		6.29		15.28		9.33		17.05
L61	FNA	20.00	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR61	19.10	95.50	5.94	88.77	5.91	77.63	3.55	90.48	0.48	75.15	0.51	85.45	26.83	91.28
	Leach Rec				11.23		22.37		9.52		24.85		14.55		8.72
L62	FNA	20.01	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR62	19.43	97.10	5.76	87.53	6.98	93.23	3.58	92.66	0.48	76.41	0.50	85.18	23.61	81.67
	Leach Rec				12.47		6.77		7.34		23.59		14.82		18.33
L63	FNA	20.00	100.00	6.39	100.00	7.27	100.00	3.75	100.00	0.61	100.00	0.57	100.00	28.07	100.00
	LR63	19.29	96.45	5.54	83.68	6.73	89.29	3.59	92.26	0.45	71.15	0.48	81.22	23.79	81.74
	Leach Rec				16.32		10.71		7.74		28.85		18.78		18.26