BENEFICIATION OF OXIDE LEAD AND ZINC MINERALS BY
SELECTIVE FLOTATION AND AMMONIA LEACHING

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SELECTIVE FLOTATION AND AMMONIA LEACHING**

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ABSTRACT

BENEFICIATION OF OXIDE LEAD AND ZINC MINERALS BY
SELECTIVE FLOTATION AND AMMONIA LEACHING

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This study was aimed to concentrate a carbonate rich lead and zinc ore by selective flotation and agitating ammonia leaching. Run-of-mine ore with 13.59% Pb and 28.31% Zn used in this study was provided from Kayseri-Develi region of Turkey. Initially the mineralogical characterization of the ore was performed using polarized microscopy and that showed cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$) are the main components in the ore together with dolomite and limonite as gangue minerals. Prior to flotation tests, effect of pH was investigated. Later, galena flotation was conducted. According to the pre-determined flowsheet, two stages (rougher+cleaner) flotation was performed and effects of collector type and dosage on grade and recovery of galena was examined. As a result of the experiments, a galena concentrate containing 75.81 % Pb was produced using 200 g/t potassium amyl xanthate (KAX) and 53 g/t F-533 as frother. For flotation of cerussite, effects of dosage and conditioning time of sulfidizing agent, collector type and dosage and desliming were investigated. At the end of the cerussite flotation tests, a concentrate was obtained having 63.25% Pb and 82.76% overall recovery. Optimum conditions for this flotation were determined as; 2000 g/t sodium sulfide (Na_2S) with 10 minutes of conditioning, 400 g/t potassium amyl xanthate (KAX) as collector and 53 g/t F-

533 as frother at pH 9.5. Desliming had negative effect on grade and recovery since Pb distributed mostly in fine sizes. As the second part of the study, effects of different ammonia contained reagents, reagent concentration and leaching duration on leaching of smithsonite ($ZnCO_3$) were examined. Within the context of the tests, ammonia (NH_3), ammonium chloride (NH_4Cl) and ammonium carbonate (($NH_4)_2CO_3$) were used at 5 M and 7 M concentrations for 30 minutes, 1 hour, 3 hours, 6 hours and 12 hours at ambient temperature. In consequence of the test results, the best result obtained as 86% Zn extraction with 7 M ammonium carbonate (($NH_4)_2CO_3$) solution and 12 hours of conditioning.

Keywords: Flotation, Ammonia Leaching, Oxide Minerals, Lead, Zinc, Smithsonite, Cerussite.

ÖZ

OKSİTLİ KURŞUN VE ÇİNKO MİNERALLERİNİN
SEÇİMLİ FLOTASYON VE AMONYAK LİÇİ İLE ZENGİNLEŞTİRİLMESİ

Talan, Deniz

Yüksek Lisans, Maden Mühendisliği Bölümü
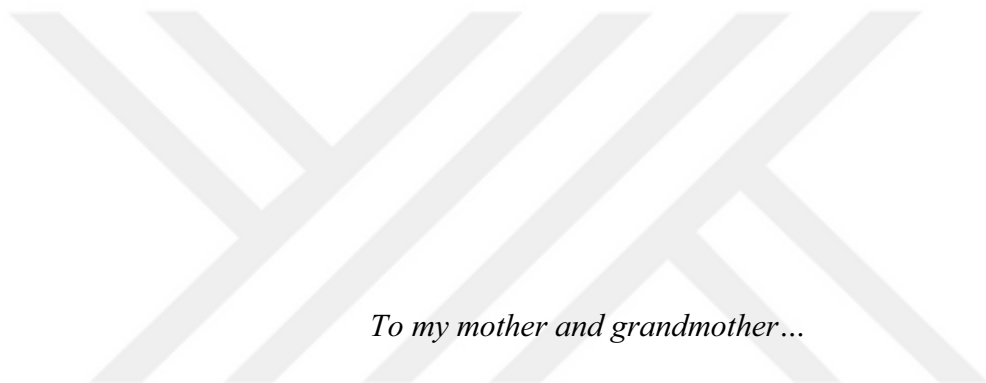
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Bu çalışmada karbonatlı kurşun-çinko cevherinin seçimli flotasyon ve karıştırmalı amonyak liçi ile zenginleştirilmesi amaçlanmıştır. Deneylerde kullanılan %13.59 Pb ve %28.31 Zn tenörüne sahip cevher Kayseri-Develi bölgesinden alınmıştır. Polarize mikroskop ile yapılan mineralojik karakterizasyon çalışmaları sonucunda seruzit ($PbCO_3$) ve simitsonit ($ZnCO_3$) cevherin ana mineralleri olarak belirlenmiştir. Gang mineralleri olarak ise dolomit ve limonit saptanmıştır. Galen ve seruzit flotasyonu testlerine başlamadan önce pH'ın etkisi incelenmiştir. Daha sonra cevherde az miktarda gözlenen galenden kurşun kazanımı için flotasyon testleri yapılmıştır. Belirlenen akım şeması çerçevesinde iki aşamalı (kaba flotasyon+temizleme) flotasyon yapılarak yalnızca toplayıcı çeşidinin galen flotasyonuna etkisi incelenmiştir. Yapılan deneylerin sonucunda %75.81 Pb içeren galen konsantresi 200 g/t potasyum amil ksantat (KAX) ve 53 g/t F-533 kullanımı ile elde edilmiştir. Seruzit flotasyonu çalışmalarında sülfürleştirici miktarı ve kondüsyonlama süresi, toplayıcı çeşidi ve şlam atmanın tenör ve verim üzerindeki etkileri incelenmiştir. Flotasyon testleri sonunda, %82.76 toplam verimle %63.25 Pb içeren seruzit konsantresi elde edilmiştir. pH 9.5'da yapılan deneylerde 10 dk kondüsyonlama süresi ile 2000 g/t sodyum sülfür (Na_2S), 400 g/t potasyum amil ksantat (KAX) ve 53

g/t F-533 köpürtücü optimum koşul olarak belirlenmiştir. Kurşunun ince tane fraksiyonlarındaki dağılımı nedeniyle şlam atmanın tenor ve verime negative etkisi olduğu belirlenmiştir. Çalışmanın ikinci kısmında, amonyak içeren farklı liç kimyasalları ile farklı konsantrasyonlarda liç süresinin simitsonit liçine etkisi incelenmiştir. Bu amaçla 30 dakika, 1 saat, 3 saat, 6 saat ve 12 saatlik liç sürelerinde amonyak (NH_3), amonyum klorür (NH_4Cl) ve amonyum karbonat ($(NH_4)_2CO_3$) 5 ve 7 M konsantrasyonlarında kullanılmıştır. Yapılan deneylerin sonucunda %86 çinko kazanımı elde edilmiştir. En yüksek sonuç 7 M amonyum karbonat ($(NH_4)_2CO_3$) ve 12 saat liç süresi ile elde edilmiştir.

Anahtar Kelimeler: Flotasyon, Amonyak Liçi, Oksitli Mineraller, Kurşun, Çinko, Simitsonit, Seruzit.

To my mother and grandmother…

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

Mineral processing is a discipline which aims to beneficiate the ores extracted from the earth crust to produce for several end uses. Since the early ages, minerals are used exceedingly in daily life and mineral processing technology is growing every day.

Lead and zinc are two of the most extensively used commodities throughout the history and have a major significance for mining and metallurgical industries. According to the data taken from the United States Geological Survey (2015), in the world, there are more than 86×10^6 tons of lead and more than 230×10^6 tons of zinc reserves. Those mineral deposits are mainly located in the USA, Australia, China, Canada and other countries. Turkey particularly has an advantage of having plenty of sulfide and oxide type lead and zinc reserves. According to data taken from the General Directorate of Mineral Research and Exploration (MTA) in 2013, lead and zinc reserves in Turkey are approximately 861 thousand tons and 2.5 million tons, respectively and their distribution with respect to the regions are presented in Figure 1.1. Approximately, 864 thousand tons of Turkey's total lead and zinc reserves consist of oxide type reserves with Pb+Zn grade greater than 7%. These are mainly located in Central Anatolia and they are presented in Table 1.1 (SOP, 2001).

Table 1.1 Oxide type reserves with Pb+Zn grade greater than 7% in Turkey
(modified from SOP, 2001)

| Region | City | County | Grade (%) | | Reserve |
			Zn	Pb	(10^3 tons)
Oxide type ores					
Central Anatolia	Kayseri	Yahyalı-Aladağ	12.9	6.9	397
	Kayseri	Yahyalı-Dereköy	25.0	10.0	60
	Kayseri	Yahyalı-Suçatı	25.0	1.0	15
	Kayseri	Yahyalı-Denizovası	16.0	4.0	10
	Kayseri	Yahyalı-Ağcaşar	22.0	3.0	20
	Kayseri	Yahyalı-Çadırkaya	20.0	2.0	10
	Kayseri	Develi-Havadan	22.0	1.0	25
	Kayseri	Zamantı	20.1	3.7	53.5
	Niğde	Çamardı-Tekneli (1)	21.5	6.0	129
	Niğde	Çamardı-Tekneli (2)	18.0	4.0	25
	Adana	Pozantı-Akdağ	22.0	2.0	15
	Adana	Tufanbeyli-Beşiktaş	13.2	4.0	49
	Adana	Tufanbeyli-Akçal	17.8	2.7	8.5
	Adana	Kozan-Horzum	28.0	1.0	20
	Konya	Bozkır	25.0	1.0	15
	Malatya	Yeşilyurt-Görgü	19.8	6.0	12
Total					**864**

Mostly, lead and zinc occur in sulfide form associated with each other and occasionally with copper and iron sulfides. Other mineralization types for lead and zinc are non-sulfide ores and mixed sulfide-oxide ores (Moradi and Monhemius, 2011). Although almost all of metallic lead and zinc production come from galena and sphalerite, non-sulfide forms also have a considerable potential for the purpose of producing lead and zinc concentrates (Snodgrass, 1986; Van Niekerk and Begley, 1991; Yin et al., 2010; Ma et al., 2011; Abkhoshk et al., 2014). Location of some

non-sulfide lead and zinc mineral deposits (smithsonite, hemimorphite, hydrozincite, cerussite, anglesite etc.) in the world is given in Figure 1.2.
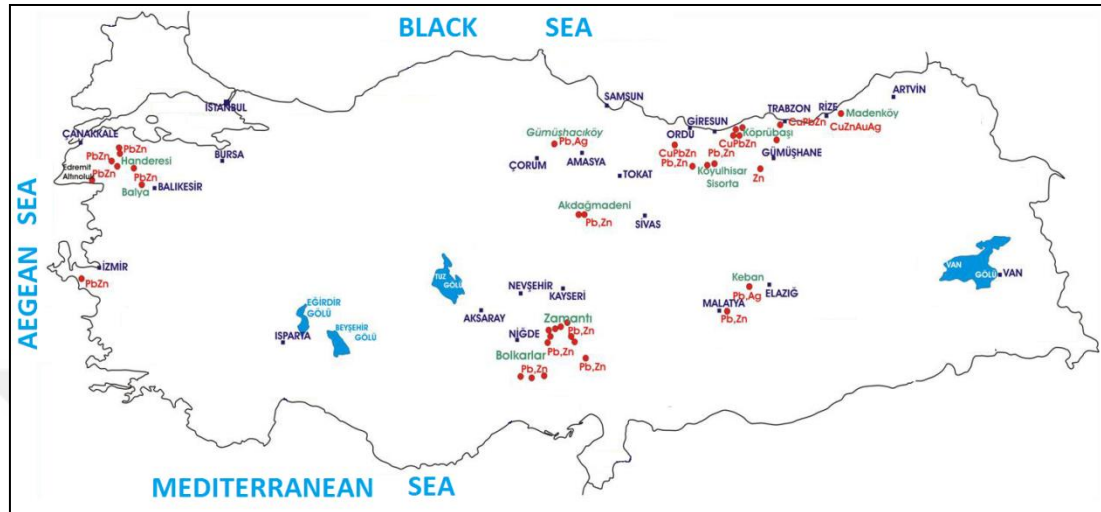
Figure 1.1 Lead and zinc mineral deposits of Turkey (modified from MTA)

Figure 1.2 Location of non-sulfide lead and zinc mineral deposits in the world (Mondillo, 2013)

With respect to world metal consumption, zinc is the fourth and it is used for various applications, such as manufacture of dry-cell battery cans, production of zinc dust and zinc chemicals, galvanizing and in textile industry (EPA, 1994; SOP, 2001; Sinclair, 2005; Chatterjee, 2007; Rüşen, 2007; Free, 2013; Ejtemaei et al., 2014). Sphalerite (ZnS) is the most known zinc mineral and almost whole zinc production is provided from sphalerite. Other sources of zinc are smithsonite, calamine, hemimorphite, zincite and etc (Energy and Environmental Profile of the U.S. Mining Industry; Sinclair, 2005). Among these, smithsonite is the most abundant one and because of the depletion of sulfide ores, production of zinc metal from zinc oxide ores became more of an issue (Rüşen, 2007; Moradi and Monhemius, 2011; Ejtemaei et al., 2014).

Because of its high density, high resistance to chemical attack, high resistance to corrosion, low melting point and softness, lead is one of the most widely used metals in the world (Snodgrass, 1986; SOP, 2001; Rüşen, 2007). Main consumption area of lead is lead-acid storage batteries. It is also used for shielding applications, in hospitals to prevent X-ray radiation to spread for covering cable and etc. due to its mentioned properties (Snodgrass, 1986; SOP, 2001; Rüşen, 2007; Chatterjee, 2007; Free, 2013). Although there are more than a hundred different lead minerals, like in zinc production, around 90% of lead is produced from its sulfide form, galena (PbS). Some other most common lead minerals are cerussite ($PbCO_3$), which is altered form of galena, anglesite ($PbSO_4$), pyromorphite ($Pb_5Cl(PO_4)_3$) and jamesonite ($Pb_2Sb_2S_5$).

Most commonly, froth flotation, which is used over a hundred years in mineral processing, is utilized in order to beneficiate lead and zinc ores (Gupta and Yan, 2006; Farrokhpay, 2011; Ata, 2012). Especially, due to their sulfur content, that increases their amenability to flotation, lead and zinc sulfide type minerals are processed with this method. Hydrometallurgical and pyro-metallurgical processes, like leaching and smelting are conducted generally for non-sulfide lead and zinc ores such as cerussite and smithsonite (Abkhoshk et al., 2014).

Even though it is generally used for concentration of galena and sphalerite, beneficiation of oxide lead and zinc minerals using flotation has also been investigated for a long time. However, because of their complex structure, high consumption of flotation reagents, surface coating issues, lower selectivity and need for complicated flowsheets, the results from such studies were ignored until recent years (Şentürk, 1987; Moradi and Monhemius, 2011; Lan et al., 2013). Recently, due to the depletion of economically extractable lead and zinc sulfides, enrichment of oxide type ores are gaining more importance (Hossein et al., 2008; Li et al., 2010; Moradi and Monhemius, 2011; Wu et al., 2013; Abkhoshk et al., 2014; Ejtemaei et al., 2014).

Other extraction methods for oxidized ores are pyrometallurgical and hydrometallurgical processes. Among these two, hydrometallurgical processes are more advantageous, since pyrometallurgical processes require higher level of energy use and the production cost is much higher as compared to hydrometallurgical processes. In addition, hydrometallurgical processes require lower temperatures and are applicable to complex ores (Habashi, 1970; Gupta and Mukherjee, 1990). More detailed comparison between pyrometallurgical and hydrometallurgical processes is provided in Table 1.2.

Leaching; a hydrometallurgical process, is generally the second option for enrichment of ores. In some cases, it may require more time such that several months to sufficiently extract the valuable part than concentrated by flotation but still due to its advantages like extracting finely disseminated particles and low grade ores that could not be floated, leaching is widely used all over the world (Meng and Han, 1996).

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Table 1.2 Comparison of pyrometallurgical and hydrometallurgical processes (Gupta and Mukherjee, 1990)

Pyrometallurgical Process	Hydrometallurgical Process
Treatment of high grade ore is more economical	Treatment of low grade ores is more economical
Generally large scale operations with high capital investment	Generally small scale operations with lower capital investment
Separation of chemically similar materials is not possible	Enables separation of chemically similar materials
Reaction rate is fast due to higher process temperatures	Reaction rate is slow due to low process temperatures
Handling of materials is problematic	Handling of materials is easily done by pipelines
Dust problem is common	No dust problem
Post-process toxic gases are common and these may require expensive control systems	Mostly no toxic gas generation
Complex engineering is not required	Complex engineering is required

In this work, the main objective is to produce lead and zinc concentrates from cerussite and smithsonite using conventional flotation and ammonia leaching techniques. The ore sample used in this study was received from Kayseri-Develi, Turkey. In this context, for flotation studies, the effects of various flotation parameters such as amount of sulfidizer, conditioning time of sulfidizer, type of collector added, pH and significance of desliming were investigated to determine optimum conditions. Furthermore, for leaching tests, by using ammonia (NH_3) and ammonia contained chemicals, which are ammonium chloride (NH_4Cl) and ammonium carbonate ((NH_4)$_2CO_3$), effects of different leaching reagent and reagent concentration and additionally duration of leaching on Zn extraction were studied.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 General

Flotation is one of the oldest mineral processing methods such that it was used for the first time by Herodotus in the fifth century B.C. for the separation of gold from sand. Later in the fifteenth century, it was used by Arabs for separation of azurite from its gangue. Then the technique has been improved by the contributions of several researchers to constitute its current form as froth flotation (Glembotskii et al., 1972). Since the nineteenth century, froth flotation is used widely for separation of complex and low-grade sulfide, oxide, nickel and gold-hosting sulfide ores, non-metallic ores and coal (Leja, 1982; Choon, 1983; Gupta and Yan, 2006; Wills and Napier-Munn, 2006; Uribe-Salas et al., 2007).

Leaching is another old beneficiation technique including dissolution of valuable metals from an ore. The history of leaching goes back to 1800's to first recover copper. Since then it is improved to recover not only low grade copper ores but also nickel, cadmium, zinc ores and precious metals. Nowadays it is commonly applied to low grade ores and also it is used to enrich flotation concentrates (Gupta and Mukherjee, 1990; Habashi, 2005).

2.2 Theoretical Background of Froth Flotation

Flotation is very applicable and effective especially for the enrichment of fine size (generally -75µm) ores depending on their differences of surface properties (Choon, 1983; Gupta and Yan, 2006; Wills and Napier-Munn, 2006). It is both a physical and

a chemical process considering flotation kinetics together with the action of reagents and surface chemistry of minerals in water (Kitchener, 1984). For that reason, flotation process is defined as physico–chemical process and basically relies on the separation of hydrophobic (aerophilic or water repellent) particles from hydrophilic (water-loving) ones by means of the attachment of hydrophobic particles to 0.1 to 5 mm diameter air bubbles. Later on, these attached particles go up under the influence of buoyancy and they form a froth zone. Then, this froth zone is collected as concentrate and the hydrophilic particles stay at the bottom as tailing (Leja, 1982; Tao et al., 2000; Gupta and Yan, 2006; Farrokhpay, 2011; Rahman et al., 2012). The schematic representation of froth flotation can be seen in Figure 2.1.
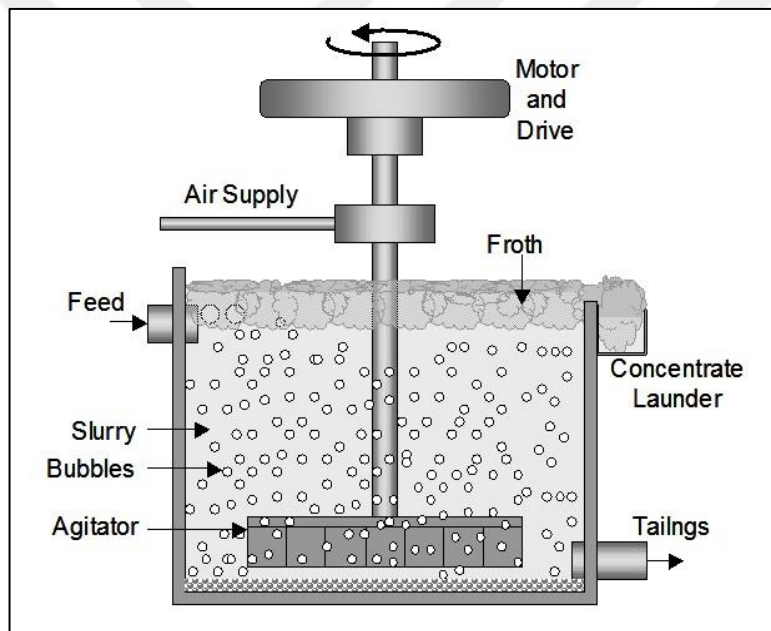
Figure 2.1 Schematic representation of froth flotation (Wills and Napier-Munn, 2006)

In flotation process, there is a three phase system consisting of solid, liquid and gas phases (Gupta and Yan, 2006; Wills and Napier-Munn, 2006; Bulatovic, 2007). In Figure 2.2, this three phase contact system is seen (Gupta and Yan, 2006).

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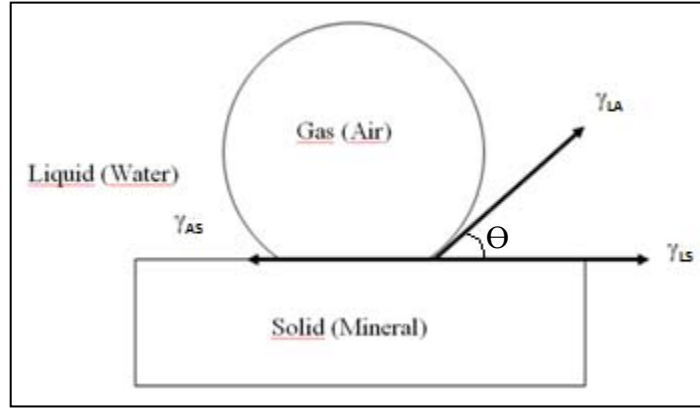
Figure 2.2 Three phase contact system

Here, the solid phase is mineral, liquid phase is water and gas phase is air. The angle between solid phase and the tangent to the liquid phase is called contact angle (θ) and it is always measured through the liquid phase (Leja, 1982; Gupta and Yan, 2006; Drzymala, 2007). Generally, contact angle shows wettability of particles where hydrophobic surfaces have a contact angle greater than 90º while hydrophilic surfaces have smaller than 90º (Gupta and Yan, 2006). This result comes from the relationship of surface tension forces seen in Equation 1, 2 and 3 (Wills and Napier-Munn, 2006; Chau et al., 2009).

$$\gamma_{A/S} = \gamma_{L/S} + \gamma_{L/A}\cos\theta \tag{1}$$

Here, γ shows the surface energies of solid-air, solid-water and air-water. The force required to de-attach bubble-particle interface is called as work of adhesion (W) and it is equal to work required to de-attach solid-air interface and produce two separate interfaces as air-water and solid-water as shown in Equation 2 (Wills and Napier-Munn, 2006).

$$W_{A/S} = \gamma_{L/A} + \gamma_{L/S} - \gamma_{A/S} \tag{2}$$

When Equation 1 and 2 combined, Equation 3 is formed and that shows the effect of contact angle for greater work of adhesion between particle and air bubble (Wills and Napier-Munn, 2006).

$$W_{A/S} = \gamma_{L/A} (1-\cos\theta) \tag{3}$$

Although, there are some naturally hydrophobic materials like coal, talc, molybdenite, graphite and sulfur, most of the minerals have hydrophilic characteristics (Gupta and Yan, 2006; Drzymala, 2007). To float hydrophilic minerals, it is necessary to use some chemicals called as flotation reagents. By using flotation reagents it is possible to change the surface characteristics through the adsorption of chemicals (Wills and Napier-Munn, 2006).

2.2.1 Flotation Reagents

The flotation reagents are divided into three groups as; collectors, frothers and modifiers (regulators). Modifiers are also divided into three sub-groups as depressants, activators and pH regulators (Gupta and Yan, 2006; Wills and Napier-Munn, 2006; Bulut and Göktepe, 2012).

2.2.1.1 Collectors

Collectors are organic compounds with the role of rendering a hydrophilic surface to a hydrophobic surface (Gupta and Yan, 2006; Wills and Napier-Munn, 2006). Collectors are classified into two as ionizing and non-ionizing according to their solubility in water. The ionizing ones are asymmetric in structure and they have a polar and a non-polar part whereas non-ionizing collectors do not have a polar part. Ionizing collectors are also divided into two as anionic and cationic collectors according to the active ion in their structure. Anionic collectors are the most widely used ones. Some commonly used anionic collectors are sulphydryl compounds or

oxyhydryl compounds and frequently used cationic collectors are amines (Choon, 1983).

2.2.1.2 Frothers

Frothers are heteropolar compounds, used to stabilize the air bubbles by reducing the surface tension at the air-water interface (Choon, 1983; Pearse, 2005; Gupta and Yan, 2006; Wills and Napier-Munn, 2006; Khoshdast and Sam, 2011). Since frothers are heteropolar, they have a polar and a hydrocarbon group where polar group interacts with water and the hydrocarbon part of the frother interacts with the air phase (Khoshdast and Sam, 2011). Although, the stabilization of froth zone depends substantially on frother type and dosage, other parameters such as gas dispersion and contact angle may also have effects on froth stability (Farrokhpay, 2011). Usually, frothers have no or very small collecting capability. On the other hand, they must have an ability to be soluble in water to be distributed equally and be fully effective. Most widely used frothers are pine oil, cresylic acid as natural reagents and methyl isobutyl carbinol (MIBC) and polyglycol ethers as synthetic reagents (Wills and Napier-Munn, 2006; Gupta and Yan, 2006). However, amount of cerylic acid to be used is much higher to reach the same recoveries with MIBC or pine oil.

2.2.1.3 Modifiers

2.2.1.3.1 Activators

Activators are used prior to collectors preparing the surface of the particle for the adsorption of the collector (Gupta and Yan, 2006).

One of the most commonly used activator is sodium sulfide (Na_2S) for changing the surface of an oxide into a sulfide form. In the reactions below, dissociation of sodium sulfide and action on a metal oxide were given (Wills and Napier-Munn, 2006).

$$Na_2S + 2H_2O \leftrightarrow 2NaOH + H_2S \qquad \qquad (4)$$

$$NaOH \leftrightarrow Na^+ + OH^- \qquad \qquad (5)$$

$$H_2S \leftrightarrow H^+ + HS^- \qquad \qquad (6)$$

$$HS^- \leftrightarrow H^+ + S^{2-} \qquad \qquad (7)$$

$$MO + S^{2-} + 2H^+ \leftrightarrow MS + H_2O \qquad \qquad (8)$$
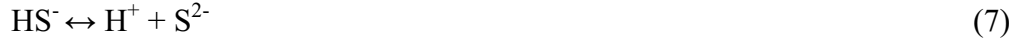
In reaction 8, MO shows an oxide surface and due to the S^{2-} ion, metal sulfide (MS) is formed.

Copper sulfate ($CuSO_4$) is another widely used activator for the activation of sphalerite (ZnS). The mechanism is explained by the following equation (Equation 9). Here, copper ions (Cu^{++}) replace zinc ions (Zn^{++}) from sphalerite lattice.

$$ZnS_{(s)} + Cu^{++}_{(aq)} \leftrightarrow CuS_{(s)} + Zn^{++}_{(aq)} \qquad \qquad (9)$$

2.2.1.3.2 Depressants

These reagents act opposite to the activators and their role is to prevent the particle to float by prohibiting the adsorption of the collector (Gupta and Yan, 2006; Wills and Napier-Munn, 2006).

Depressants are divided into two as organic and inorganic. Starch, dextrin, tannin, quebracho can be given as examples for organic depressants while ammonia, calgon, sodium silicate, cyanide, chromate and phosphates can be given as examples for inorganic depressants (Drzymala, 2007).

2.2.1.3.3 pH Regulators

The pH of the pulp is a very important parameter and most of the time it is the first thing to be controlled for a successful flotation process. Generally, flotation is conducted in alkaline medium because alkaline medium reduces corrosion of cells and pipe work and also most of the reagents are more effective in alkaline medium. Alkaline pH is provided by using lime, caustic soda, soda ash etc. When lower pH is needed, sulfuric acid can be used (Leja, 1982; Gupta and Yan, 2006; Wills and Napier-Munn, 2006).

2.3 Theoretical Background of Column Flotation

Invention of column flotation goes back to 1960s by Pierre Boutin and Remi Trembley (Gürsu, 1998) and flotation columns were introduced to the industry first by Column Flotation Co. in Canada (Finch, 1995).

Columns were developed because fine sized gangue particles were going to the concentrate due to the turbulence caused by stirring in mechanical cells (Hacıfazlıoğlu, 2007). This invention considered such an important one in mineral processing industry and lots of studies concluded that flotation columns give better results than a conventional cell-type flotation especially in the cleaning stages. So that replacing of columns instead of conventional cells are increasing in industry. (Sastri, 1998; Uribe-Salas et al., 2007; Kursun ve Ulusoy, 2012). An example to this is Rajpura Dariba mine in India where nine mechanical cells were replaced with two columns to increase zinc grade (Mittal et al., 2000).

Apart from some advantages like lower cost, more productivity, better control, less wearing, less floor requirement, according to some researchers the most important feature of column flotation equipment is the washing of froth (Finch, 1995; Rubio, 1996; Gürsu, 1998; Sastri, 1998; Tao et al., 2000; Hacifazlioglu and Sutcu, 2007).

As it can be seen in Figure 2.3, there are two main zones in flotation column: one of them is known as collection zone or flotation zone and the other zone is called

cleaning zone or froth zone. In collection zone feed is introduced to flotation column from approximately 2/3 of total height and air is introduced via sparger. The purpose of this sparger is that the particles which flow downwards collide with rising air bubbles (Gürsu, 1998; Hacifazlioglu and Sutcu, 2007). In cleaning zone froth formed by rising bubbles is washed and washed froth gathers in the launder to be taken as concentrate while rest of the pulp stays at the bottom and discharged as tailing (Rubio, 1996; Sastri, 1998; Ata et al., 2002; Honaker et al., 2006; Smith , 2012).
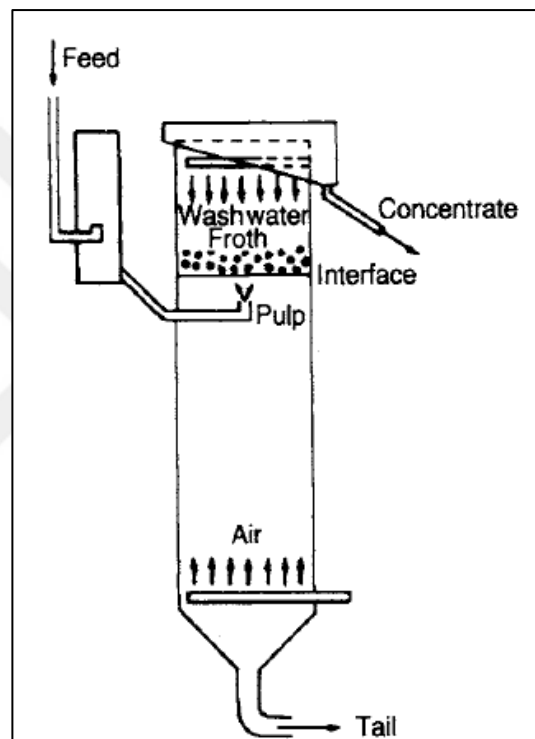
Figure 2.3 Flotation column (Wills and Napier-Munn, 2006)

2.4 Flotation of Oxide Lead and Zinc Ores

Beneficiation of oxides using flotation is rather hard compared to sulfides since oxides can dissolve easily and their surfaces become hydrated easily (Herrera-Urbina et al., 1998). Solubility product constants for smithsonite ($ZnCO_3$) and cerussite ($PbCO_3$) are 1.46 x 10^{-10} and 7.40 x 10^{-14}, respectively (Fa et al., 2005). Also during flotation of oxides, slimes coat the surface of the particles and prevent their

floatability. Since oxides can dissolve easily, collectors react with metal cations in the pulp, increasing the consumption of reagents (Marabini et al., 2007; Abkhoshk et al., 2014). In addition to these, there are no direct-acting collectors for oxides to produce single-metal concentrates (Marabini et al., 2007; Li et al., 2010).

To float oxides, either fatty acids or amines can be used as collectors without making any activation, or as a second option, first a sulfidizing agent then thio collectors can be used (Somasundaran and Lou, 1999). Among these two methods, most widely used one is flotation with a sulfidizer (Li et al., 2010). Since flotation with a fatty acid or amine without making any activation is not a very selective process, also it can also be carried out just for a couple of ores and requires high amount of reagents (Leja, 1982; Somasundaran and Lou, 1999; Drzymala, 2007).

In addition, there are other types of collectors called chelating reagents. Chelating collectors were introduced to the industry by Italian researchers. These reagents are capable of making bonds with metal ions via functional groups with the formation of rings called as chelates. Chelates have high stability and selectivity depending on electronic and steric forces. There are two classes of chelating reagents as MercaptoBenzoThiazole (MBT) and AminoThioPhenole (ATP). MBT type chelating reagents are used only for lead minerals, where ATP types chelating reagents can be used both for lead minerals and zinc minerals (Marabini et al., 2007; Liu et al., 2012). Although they have a potential to be used for oxide lead and zinc minerals, due to their higher costs, they are not preferred in industrial scale (Wills and Napier-Munn, 2006).

Sulfidizers are used to convert the surfaces of oxide lead and zinc particles into lead sulfide and zinc sulfide thanks to the sulfide ions distributed in an aqueous solution. Later, they can be treated easily with flotation reagents (Herrera-Urbina et al., 1998; Drzymala, 2007). Sodium sulfide or sodium hydro-sulfide is used as sulfidizing agent. With sulfidization process, surface of oxide mineral is converted to sulfide as a result of the dissolution of Na_2S into HS^- and S^{2-} ions (Fa et al., 2005). The

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sulfidization reaction of cerussite using sodium sulfide can be seen in the Equations 10-13 (Wills and Napier-Munn, 2006).

$$Na_2S + H_2O \leftrightarrow NaHS + NaOH \qquad (10)$$

$$PbCO_3 + 3\ NaOH \leftrightarrow H_2O + Na_2CO_3 + NaHPbCO_2 \qquad (11)$$

$$NaHS + NaHPbO_2 \leftrightarrow 2NaOH + PbS \qquad (12)$$

$$Na_2S + PbCO_3 \leftrightarrow Na_2CO_3 + PbS \qquad (13)$$
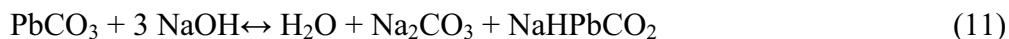
It is known from previous studies that excess amount of sulfidizer may have negative effect on oxide minerals especially on lead oxide (Bulatovic, 2010). For that reason amount of sulfidizer must be considered with care. Because excess amount of sulfidizer may prevent collector adsorption. Increase in pulp alkalinity causes formation of more HS^- and S^- ions and thus prevent collector adsorption (Wills & Napier-Munn, 2006).

After sulfidization, either phosphine based, ditiophosphate type, or xanthate type collectors can be used for oxide lead minerals (Önal et al., 2005). For flotation of oxide zinc minerals, amines can be used. Mercaptans can also be used as secondary choices for both lead and zinc oxide minerals but, especially for zinc oxide, amine type collectors give better results (Bulatovic, 2010).

For flotation of oxide zinc minerals, conditioning with a sulfidizer then collecting with amine can be improved by adding copper sulfate ($CuSO_4$) either prior or after conditioning with a sulfidizer. If it is added prior to sulfidizer, then pulp must be heated to 50–60 ºC while conditioning with the sulfidizer (Bulatovic, 2010). Slime coating is another major problem especially for flotation of oxide zinc minerals and desliming is an essential step. However, this reduces amine adsorption, consequently increases reagent consumption (de Wet and Singleton, 2008).

2.5 Theoretical Background of Leaching

Leaching or in other words dissolution can be defined as a solid–liquid mass transfer process since its main aim is to dissolve the components of the ore by using different lixiviants (Habashi, 1970). It is generally applied to oxidized ores, sulfide ores, ores that contain precious metals and concentrates or tailings of flotation. The process can take place in both ambient and elevated temperatures (Gupta and Mukherjee, 1990; Vignes, 2011).

2.5.1 Leaching Methods

Leaching methods can differ considering the mineral deposit to be treated. Some of the mineral deposits can be treated in situ but some of them may need transportation for leaching (Gupta and Mukherjee, 1990).

2.5.1.1 In Situ Leaching

In situ leaching or solution mining is the method which the deposit is not transported. A solution is pumped through fractures and metal is recovered (Figure 2.4). It is a cost friendly process and also it does not require surface disturbance compared to other leaching methods (Habashi, 1970). One disadvantage of this method is channeling which prevents uniform distribution of the solution that is pumped through fractures. Apart from that, although, it is not used in large scale operations, it is still used successfully on mined-out bodies and on bodies with low grade (Gupta and Mukherjee, 1990; Free, 2013).
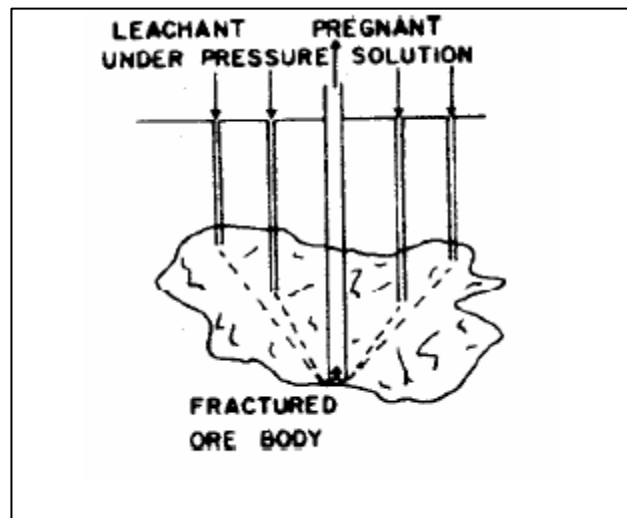
Figure 2.4 Schematic representation of in situ leaching (Hoşten, 2016)

2.5.1.2 Heap Leaching

Heap leaching method is generally applied to low and medium grade ores. This method is alike in situ leaching but in this case, ore is removed from the mine site and transported to slightly inclined ground to form heaps. The ground under heaps is called as leach pad which consists of several liners. When the ore is piled carefully and uniformly, solution is sprayed from top and the pregnant solution is allowed to be collected in basins at the end of the piles. Despite being a very slow process, heap leaching is a simple and widely used leaching method (Figure 2.5) (Gupta and Mukherjee, 1990; Free, 2013).
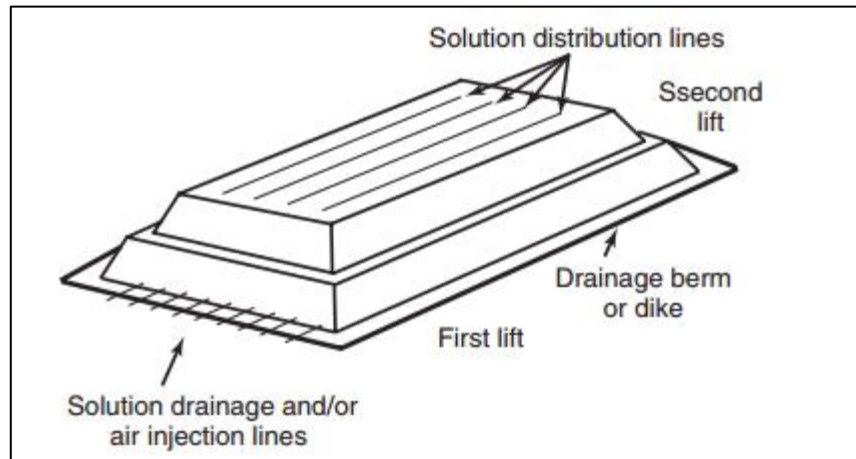
Figure 2.5 Schematic representation of heap leaching (Free, 2013)

2.5.1.3 Dump Leaching

Dump leaching is mainly used for the treatment of sulfide-bearing ores. The ore is transported from mine site and poured on an impermeable ground to form cones. As seen in Figure 2.6 leach solution is sent starting from the top and it is allowed to percolate till the end of the dump. Effective air circulation, effective bacterial activity and high solution–particle contact are the main parameters that affect the efficiency of dump leaching (Gupta and Mukherjee, 1990; Free, 2013).
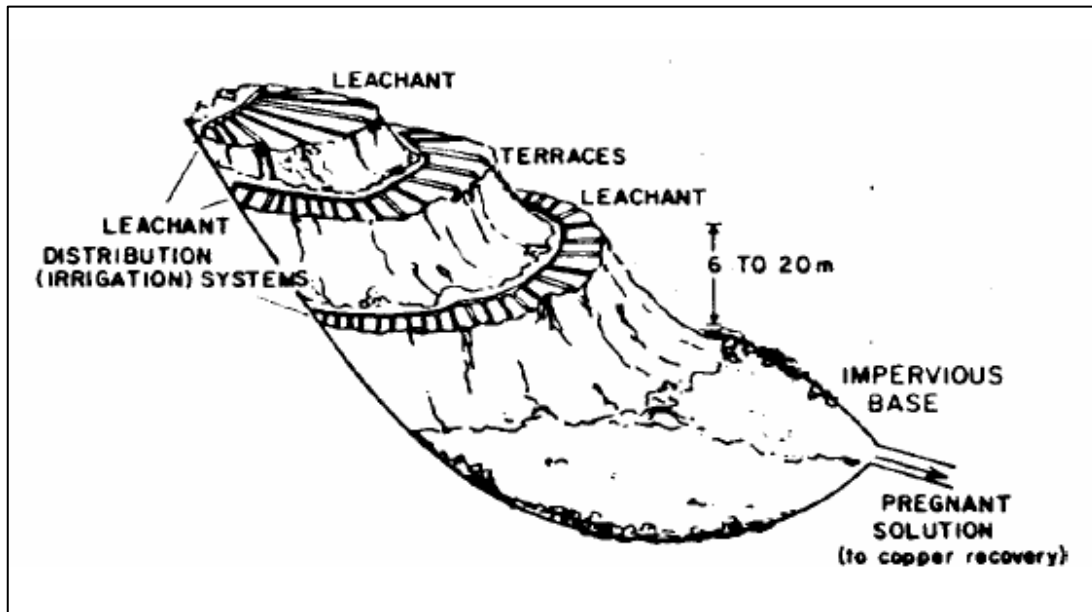
Figure 2.6 Schematic representation of dump leaching (Hoşten, 2016)

2.5.1.4 Vat Leaching

This leaching method is conducted in series of rectangular leaching vats with countercurrent principle. In this method, the material does not move as different from the most countercurrent techniques and solution percolates through the material (Gupta and Mukherjee, 1990). Lower solvent consumption and producing high grade pregnant solution are the two main advantages of vat leaching (Habashi, 1970). In Figure 2.7, simplified vat leaching system is presented.
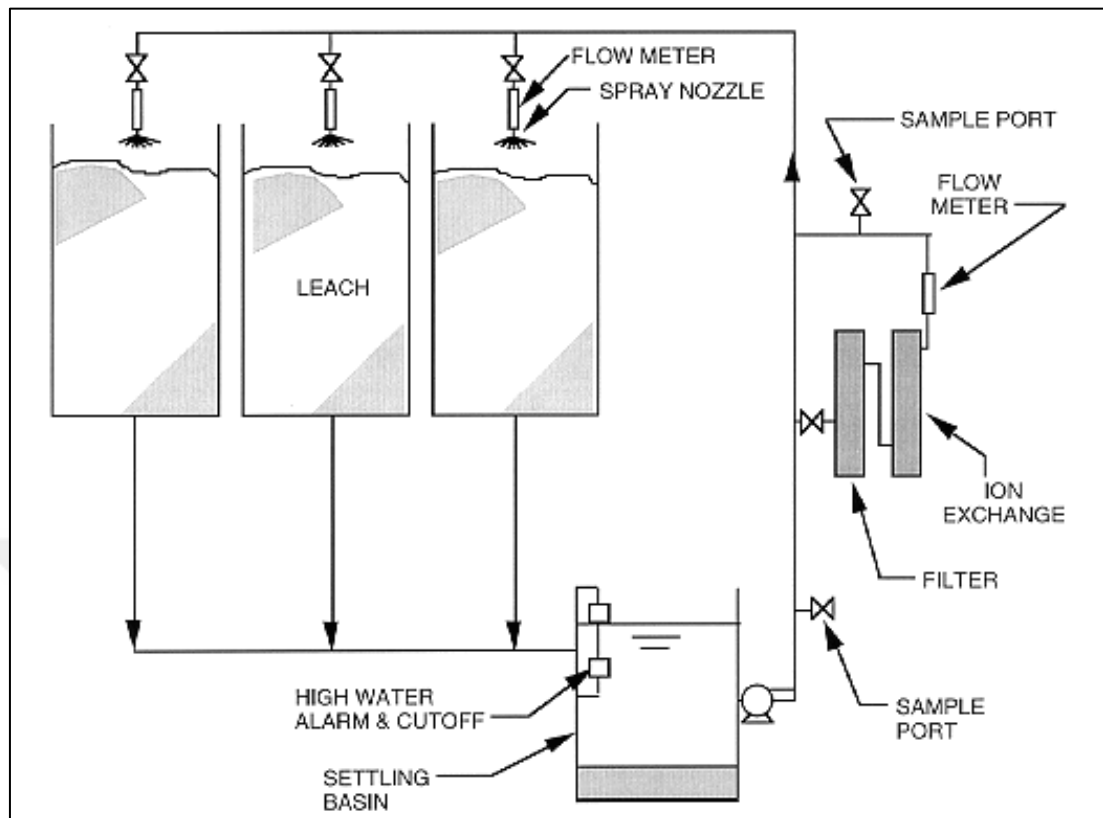
Figure 2.7 Schematic representation of vat leaching (Cummings and Booth, 1997)

2.5.1.5 Agitated Leaching

The ore to be leached is treated in series of agitated vessels. Dissolution can be either batch or continuous (Gupta and Mukherjee, 1990). Agitation action can be performed by compressed air, mechanical impeller or combination of these two (Habashi, 1970). The schematic representation of mechanical agitation is seen in Figure 2.8.a and schematic representation of pneumatic agitation is provided in Figure 2.8.b, respectively.
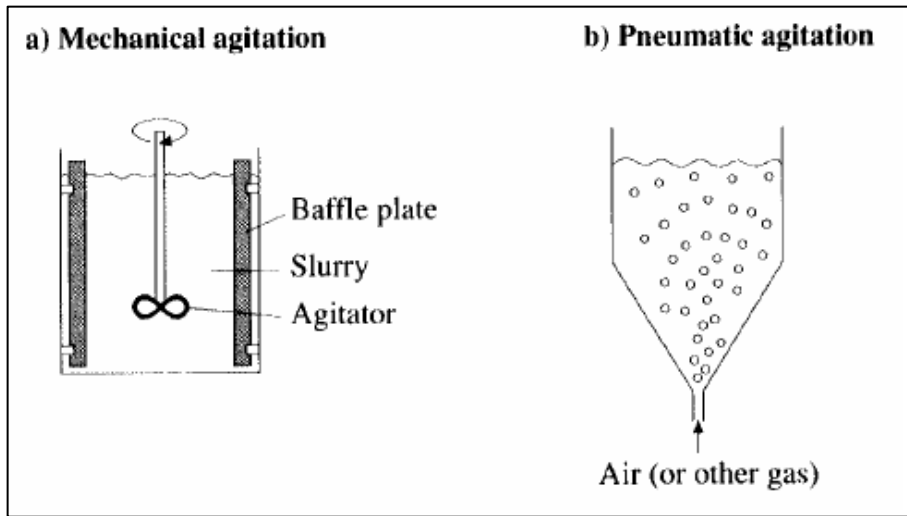
Figure 2.8 Schematic representation of agitated leaching (Hoşten, 2016)

2.5.1.6 Pressure Agitated Leaching

Pressure agitation leaching is performed in autoclaves at high temperatures and pressure. Nickel-cobalt sulfides along with sulfides and uranium ores can be treated with this method (Hoşten, 2016). Also high pressure acid/autoclave leaching has some advantageous over ambient conditions such as high removal of iron and less oxygen consumption (Free, 2013). Pressure leaching in two stage autoclave is presented in Figure 2.9.
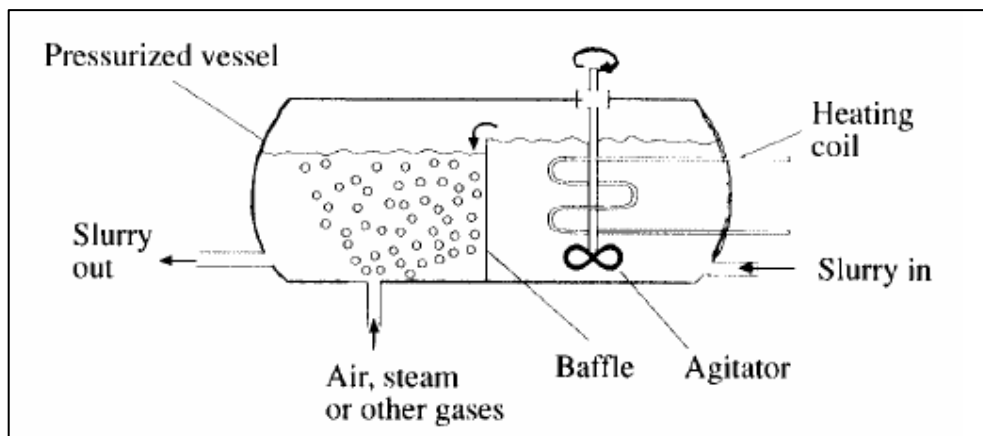
Figure 2.9 Pressure leaching in two stage autoclave (Hoşten, 2016)

2.5.2 Leaching Reagents

Main properties of a good leaching agent are listed as follows (Gupta and Mukherjee, 1990);

- It must dissolve the valuable part in the ore fast while leaving unwanted parts undissolved.
- It must be recovered at the end of the process for reutilization.
- It must be cheap and easily available when needed.

Classification of leaching reagents is given in Table 2.1.

Table 2.1 Classification of leaching reagents (Gupta and Mukherjee, 1990)

Category	Reagent	Area of use
Acids	Dilute H_2SO_4 Dilute H_2SO_4+oxidant Concentrated H_2SO_4 Nitric acid	Copper oxide, zinc oxide, sulfides of Cu, Ni and Zn Copper sulfide concentrates, laterites, sulfides of Cu, Ni, Mo scrap, uranium concentrates
Alkalies	Hydrofluoric acid Hydrochloric acid Sodium hydroxide Sodium carbonate Ammonium hydroxide + air	Columbite – tantalite ore Ilmenite, nickel matte Bauxite Uranium oxide Nickel sulfide, copper sulfide, reduced laterite
Salts	Ferric chloride/sulfate Cupric chloride Sodium or potassium cyanide + air Ferrous chloride + air	Base metal sulfide concentrates Base metal sulfide concentrates Gold and silver ores Nickel sulfide

Table 2.1 (cont'd) Classification of leaching reagents (Gupta and Mukherjee, 1990)

Category	Reagent	Area of use
Aqueous chlorine	Aqueous chlorine	Sulfide concentrates of Cu, Ni, Zn and Pb
Water	Water	Sulfates and chlorides, sodium vanadate, molybdate, tungstate

Although sulfuric acid is the cheapest acid among the others given in Table 2.1, some disposal and health problems occur when it is used for an ore that contains high amounts of iron or radium. Formation of ferrous sulfate, when it is used for high iron contained ore, creates disposal problems and its use for high radium content ores, such as uranium ores, forms radium sulfate which causes health problems. Two of foremost advantages of alkalies (bases) over the other leaching reagents are; they are more selective and they reduce the corrosion problem significantly (Habashi, 1970).

2.6 Ammonia Leaching of Zinc Oxide

Zinc oxide ores can be beneficiated using flotation and leaching processes. Even though leaching method is more effective, because of high consumption of chemicals, flotation prior to hydrometallurgical processes is preferred. Also, hydrometallurgical processes are preferred instead of pyrometallurgical ones due to high smelting costs and strict regulations about disposal and environment (Ma et al., 2011; Moradi and Monhemius, 2011; Abkhoshk et al., 2014).

It is a known fact that sulfuric acid is the most commonly used leaching agent. But in recent years, because of some drawbacks of acid leaching such as silica releasing into solution and causing silica gel forming, many researches had been performed using different chemicals like ammonia, ammonium salts, nitric acid, chlorides, caustic soda and etc. (Ju et al., 2005; Liu et al., 2012; Abkhoshk et al., 2014). Among

these chemicals, due to some advantages such as low corrosion, low toxicity and low pollution, usage of ammonia and ammonium salts has been increased (Moghaddam et al., 2005; Wang et al., 2008; Ma et al., 2011; Radmehr et al., 2013).

Composition of ammonia was introduced for the first time by Claude Louis Berthelot in 1777. Ammonia was first commercially produced during the 1800's as the by-product of gas manufacturing through the destructive distillation of coal (Meng and Han, 1996).

At the beginning, ammonia leaching was developed to recover copper. There are several different ammonia containing processes for copper treatment. The common one is "Sherritt Gordon Process" which applies high temperature to convert sulfides to oxides to make them dissolve easily in ammoniacal solution. Another process called "The Arbiter Process" was developed to recover copper from copper, chalcocite, bornite and other precipitated copper containing concentrates (Meng and Han, 1996; Radmehr et al., 2013).

In 1924, a new process called "Caron Process" was developed to treat nickel and cobalt in addition to copper. Another process was developed by INCO of Copper Cliff to successfully extract nickel, cobalt and copper from flotation concentrates (Meng and Han, 1996; Radmehr et al., 2013).

Additionally, due to its many advantages, usage of ammonia expanded to treatment of zinc, molybdenum, precious metals and so on. The researchers that observed dissolution of zinc in ammoniacal solutions stated that dissolution rate of zinc has two behaviors with respect to ammonia concentration. The first behavior is that dissolution rate of zinc is constant as a function of leaching time at high concentrations such as greater than 0.25 M. The second behavior shows that the dissolution rate is decreasing with time at low ammonia concentrations (Meng and Han, 1996).

Ammonia is a very soluble chemical in water and it is colorless in both solid, liquid and gaseous states (Meng and Han, 1996). Some of the physical properties of ammonia are given in Table 2.2.

Table 2.2 Physical properties of ammonia (modified from Meng and Han, 1996)

Melting Point	-77.74 °C
Boiling Point	-33.42 °C
Viscosity	0.001350 poise
Critical Temperature	132.9 °C
Critical Pressure	11.379 MPa
Entropy	192.67 J/deg. mole
VaporPressure (0°C)	429.94 kPa
Density (at -30°C)	0.6777 g/cm^3
Density (at -70°C)	0.7253 g/cm^3

When ammonia dissolves in water, it forms ammonium hydroxide. Through hydrogen bonding, two substances react with each other to form NH_4^+. Reactions between smithsonite and ammonia in aqueous solution are seen in Equation 14 and 15.

$$NH_3 + H^+ \leftrightarrow NH_4^+ \tag{14}$$
$$ZnCO_3 + 4NH_4OH \leftrightarrow Zn(NH_3)_4CO_3 + 4H_2O \tag{15}$$
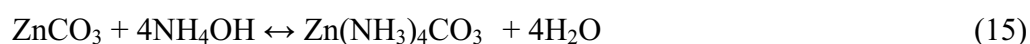
2.7 Previous Studies

Even though flotation of oxide lead and zinc minerals is relatively harder compared to flotation of sulfide ores, according to the previous studies, it was resulted that flotation can be applied for these minerals to produce sufficient lead and zinc concentrates in terms of sufficient grade and recovery (Hosseini and Forssberg, 2007).

Yang et al., (2013) performed a study using a complex ore sample, containing 2.84% Pb and 3.22% Zn and 99.5g/t Ag. For lead oxide flotation, 2000g/t sodium sulfide was determined to be the optimum amount to be used as a sulfidiser, and mixture of 60g/t ethyl xanthogenate with 50 g/t butyl amine was determined as optimum collector amount. For zinc oxide flotation, a new complex reagent mainly composed of amino alkyl ketone called KZF was used. At the end, a lead concentrate with 23.41% Pb and a zinc concentrate with 32.65% Zn were produced. Lead and zinc recoveries were 86.75% and 80.11%, respectively.

Another study was practiced to see the effect of sulfidizer on pulp potential and the effect of collector on flotation of both galena and cerussite. All experiments were conducted at pH 9.5 and during the experiments, sodium sulfide was used as sulfidizer and amyl xanthate was used as collector. From the experiments it was seen that the amount of sulfidizer is a critical parameter for cerussite flotation. When the sodium sulfide dosage is high, pulp potential shifts to decreasing flotation conditions that means mineral was depressed. Optimum sulfide dosage for cerussite was determined as 5×10^{-5} mol/dm^3. Also, the results showed that collector addition affects flotation behavior, and optimum collector dosage for this cerussite sample was determined in the potential range of -100 mV to 150 mV. In this study, galena and cerussite were also floated without the help of a collector after using sulfidizing agent, but the results were not sufficient (Herrera-Urbina et al., 1999).

In the study conducted by Shu-Juan et al., (2014) the aim was to get lead and zinc concentrates from flotation tailings which contain 0.58% Pb and 2.59% Zn using flotation process. In addition to the proven possibility of producing lead and zinc concentrates from tailings, it was also shown that sodium sulfide amount is a crucial point for cerussite in terms of grade and recovery. Experiments showed that, after a certain amount of sodium sulfide (which was 600 g/t for this ore), grade and recovery values of lead concentrate were decreasing. Also, zinc grade in lead concentrate was increasing with excess sodium sulfide amount. For flotation of zinc, amount of sodium sulfide was again determined as a crucial parameter. As a result of the study

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a lead concentrate containing 48.30% Pb with 65.41% recovery and a zinc concentrate containing 42.24% Zn with 84.69% recovery were produced.

Shahsavari et al., (2010) conducted a study with an ore containing 18.59% Pb and 1.81% Zn. The study was focused on lead oxide flotation since zinc was not able to be floated in any condition. For lead oxide flotation, several parameters were investigated and it was resulted that a concentrate containing 72.3% Pb with 73% recovery can be produced using 500 g/t Na_2SiO_3, 9500 g/t Na_2S, 600 g/t KAX and 20 g/t MIBC.

Effects of some flotation parameters on flotation of an ore which contains 20-22% smithsonite were observed by Ejtemaei et al., (2011). The highest recovery obtained for cationic flotation was 87% and optimum conditions were determined as 800 g/t Armac C and 3000 g/t Na_2S at pH 11. Also it was pointed out that for smithsonite flotation temperature and desliming have important effects and temperature must be around 30-40 ºC. Adequate grade and recovery values could not be obtained by anionic flotation. Using mixed collectors (Armac C + KAX) with 8:1 ratio at pH 11 gave best result as 64% recovery and 31% Zn grade. Hosseini and Forssberg, (2007) studied the effect of using anionic/cationic mixed collector (Potassium amyl xanthate+Dodecylamine) on flotation of smithsonite. The test sample containing 58.50% Zn was provided from Angooran region of Iran. As a result of their research, using mixed collector increased smithsonite recovery dramatically to 97%.

A study was conducted with a carbonate-hosted lead and zinc ore with 11.27% Zn and 3.45% Pb, respectively. The test sample was sulphidized prior to flotation experiments for 240 minutes at 200°C in a 2 L autoclave. After pre-sulphidization stage a lead concentrate containing 48.88% Pb with 87.67% yield and a zinc concentrate including 59.78% Zn with 89.75% yield were produced. For lead flotation, 28000 g/t CaO, 1750 g/t $ZnSO_4$, 225 g/t KAX, 225 g/t SN and 63 g/t pine oil, for zinc flotation, 2000 g/t Na_2CO_3, 1400 g/t $CuSO_4$, 505 g/t KAX and 63 g/t pine oil were used (Li et al., 2010).

Another series of experiments were performed by Fa et al., (2005) to produce lead and zinc from oxide and oxide-sulfide mixed ore containing 1.64% Pb and 10.76% Zn, respectively. For the study, a flowsheet which was consisting of sulfide flotation, desliming and oxide flotation was developed. Within the scope of the tests, effects of sodium sulfide dosage, pulp density, desliming and temperature were investigated. Sodium sulfide dosage was changed from 500 to 1250 g/t for cerussite flotation and 1500 to 4500 g/t for smithsonite flotation. As a result of the tests, it was stated that use of high amounts of sodium sulfide give better results on both cerussite and smithsonite flotation. The results of the tests conducted to observe the effect pulp density, it was determined that optimum mass concentration must be around 35–45%. Results were not sufficient in terms of grade and recovery when pulp density was below 25%. In addition to these, optimum temperature range for flotation of cerussite and smithsonite was stated as 25-40ºC. Moreover, effect of desliming was investigated by siphon and hydrocyclone methods and it was concluded that desliming was necessary for both cerussite and smithsonite flotation. Also using siphon method over hydrocyclone, loss of Zn into the slimes was decreased. At the end of the experiments a cerussite concentrate with 16.90% Pb and a smithsonite concentrate with 36.28% Zn were produced.

Şentürk et al., (1993) studied with a composite sample taken from Kayseri, Turkey. The lead and zinc grade of the composite sample were 6.69% and 17.1%, respectively. Aim of the study was to investigate the effects of flotation parameters on cerussite and smithsonite flotation. As a result of the experiments a lead concentrate with 70.7% Pb at 74.7% recovery was obtained. Optimum flotation conditions for cerussite flotation were determined as 3000 g/t Na_2S, 300 g/t KAX, 50 g/t pine oil with 10 minutes of flotation. Optimum flotation conditions for smithsonite flotation were determined as 3000 g/t Na_2S, 700 g/t Amin D-Acetate with 10 minutes of flotation and with these conditions a zinc concentrate with 35.19% Zn at 49.09% recovery was produced.

Navidi Kashani and Rashchi, (2008) used tailings of lead flotation containing approximately 35% Zn to produce zinc concentrate. In this study, effects of various flotation reagents like sulfidizing agent, amines, dispersants and flocculants were investigated. At the end of the experiments it was seen that amine dosage at a certain point increases the Zn grade but more than 365 g/t, grade of Zn was decreasing. Effect of sulfidizing agent, Na_2S, showed the same trend as amine dosage. When it was increased to 3400 g/t, Zn grade increased but after that level, Zn grade did not change. Additionally, hexametaphosphate gave better results as dispersant and flocculant is not an effective reagent for this ore. With hexametaphosphate, zinc recovery was increased to 70% and the highest zinc grade obtained with hexametaphosphate was 40% Zn. Also, for most of the studies conducted to produce zinc concentrate from smithsonite it was stated that desliming is a detrimental step but for this ore since most of the smithsonite particles were fine, desliming could not be used to increase the recovery.

Another study was also conducted by Mehdilo et al, (2014) to recover zinc from tailings of cerussite flotation which contain 21.7% Zn. As collectors alkyl amine acetates which are coco alkyl amine acetate (Armac C) and tallow alkyl amine acetate (Armac T) were used. Among these Armac T acted relatively better than Armac C but mixture of them acted much better than each of them alone. The best result was obtained was 42.3% Zn with 94.4% recovery using 1:6 Armac C:Armac T ratio at pH 11.

Farag et al., (2011) made a study about enrichment of non-sulfide zinc ore by using gravity separation techniques like shaking table and Falcon concentrator. The test sample was containing 47.5% ZnO and 1.55% PbO. As a result of the experiments, shaking table gave better result in terms of both grade and recovery. According to the optimum conditions obtained from shaking table and Falcon concentrator two concentrates containing 62.2% Zn and 54.85% Zn with 93.8% recovery and 76.6% recovery were produced respectively.

In a study conducted by Kurşun and Ulusoy (2012) a sample taken from flotation circuit of GESOM A.Ş. was used and the sample were containing 3.23% Pb, 0.52% Cu and 2.71% Zn. Flotation column was used to beneficiate this complex ore and the aim was to observe the effects of some operational parameters. For the experiments, one stage rougher, three stages of scavenger and three stages of cleaning were followed. The results showed that superficial feed rate, superficial air rate, superficial wash water rate, frother concentration and the porosity of the sparger have significant effects on performance of column. After the experiments a zinc concentrate containing 58.81% Zn with 74.21% recovery was produced.

Smith, (2012) made some experiments to observe the effects of water and air flow rates, pH and frother concentration on froth formation in flotation column. Effects of these parameters were investigated one at a time by keeping all other conditions constant. The results showed that froth formation increases with increasing water flow rate till a certain amount because it was seen that excess amount of water may break the bubbles. When air flow rate increase, froth height was also increase but when air supply turned off, froth zone disappears. Like in all flotation experiments, pH was an important parameter here and to a certain degree of pH, froth formation was increasing then it started to decrease.

Even though producing sufficient zinc concentrates from oxide zinc minerals using flotation technique is possible, in some cases because of complex structure of oxide minerals flotation technique becomes less effective. At that time hydrometallurgical methods are used instead of physical separation. Nevertheless sulfuric acid is used predominantly for hydrometallurgical extraction of oxide zinc ores, usage of ammonia and its salt is gaining more importance compared to past.

Ju et al., (2005) conducted a study with an ore containing 30.28% Zn to observe dissolution kinetics of smithsonite in ammonium chloride (Equations 16-19). They examined the effect of particle size, reaction temperature and ammonium chloride concentration. As a result of their study, 91% Zn was extracted using 84-110 μm

sized particles at 90 ºC for 240 minutes with 5 M ammonium chloride solution. In all experiments solid/liquid ratio was taken as 1:10.

$$NH_4Cl \leftrightarrow NH_3 + Cl^- + H^+ \tag{16}$$

$$ZnCO_3 + 2H^+ \leftrightarrow Zn^{2+} + CO_2 + H_2O \tag{17}$$

$$Zn^{2+} + (NH_3)_{(aq)} \leftrightarrow Zn(NH_3)^{2+} \tag{18}$$

$$Zn(NH_3)_2{}^{2+} + 2Cl^- \leftrightarrow Zn(NH_3)_2Cl_2 \tag{19}$$

Effects of leaching time, alkaline concentration, temperature, and solid/liquid ratio on extraction of low grade complex ore with 13% Zn were investigated by Ma et al., (2011). As leaching reagents, ammonia–ammonium carbonate and ammonia-ammonium chloride were used. The tests were carried out with 50 g of sample in a flask. At the end of the experiments 43.07% Zn extraction was achieved with 5 M ammonia–ammonium chloride solution at 30 ºC for 3 hours with 4:1 solid/liquid ratio.

By using ammonium carbonate, determination of optimum leaching conditions for high silica contained zinc ore (35.1% Zn) was investigated by Moghaddam et al., (2005). Taguchi method was preferred during this study and results showed that optimum temperature is 45 ºC with 3 moles of ammonium carbonate and 45 minutes leaching time. At these conditions approximately 92% extraction is achieved.

Another research carried out by Wang et al., (2008), ammonium chloride was used to recover low grade zinc oxide ore. In this study, effects of particle size, temperature and concentration of ammonia-ammonium chloride were examined. In all of the experiments, solid/liquid ratio was taken as 1:10. The results showed that extraction efficiency decreased with the increasing in particle size and optimum particle size was determined as 69 μm. Optimum temperature for leaching was determined as 80 ºC although increasing from 40 to 80 ºC does not have a significant increase other than 3%. Optimum ammonium to ammonia ratio was determined as 2:1.

Hurşit et al., (2009) studied with a test sample containing 57.28% ZnO provided from Kayseri, Turkey. The study aimed to extract Zn with an organic leaching reagent, gluconic acid and to investigate the effects of leaching parameters on dissolution rate of smithsonite. The experiments showed that the dissolution rate was not a stirring speed dependent reaction. On the contrary, it was found that increasing in acid concentration at a certain value (1.25 M) and fine sizes increased the dissolution rate of the sample. Additionally, increase in temperature resulted with rapid increase in Zn dissolution. The reactions that take place between smithsonite and gluconic acid are given in Equations 20-22.

$$2HC_6H_{11}O_7 \leftrightarrow 2H^+ + 2HC_6H_{11}O_7^- \tag{20}$$

$$ZnCO_3 + 2H^+ \leftrightarrow Zn^{2+} + CO_2 + H_2O \tag{21}$$

$$ZnCO_3 + 2HC_6H_{11}O_7 \leftrightarrow Zn^{2+} + 2C_6H_{11}O_7^- + CO_2 + H_2O \tag{22}$$

Another study leaching of a calcined smithsonite sample (10.15% Zn) with sodium hydroxide as the leaching reagent was studied (Zhang et al., 2013). Aims of the study were to observe the effects of leaching time, leaching temperature, solid/liquid ratio, calcination temperature and alkaline concentration. In the study, smithsonite decomposed to ZnO in 2 hours at 400℃. After that temperature unwanted compositions take place so that extraction rate decreases. To extract more than 92% of Zn, optimum conditions were determined as 20% NaOH solution with 80:1 solid/liquid ratio at 100 ºC for 4 hours. The reaction of ZnO with OH⁻ ions to produce $Zn(OH)_4^{2-}$ is given in Equation 23.

$$ZnO + 2OH^- + H_2O \leftrightarrow Zn(OH)_4^{2-} \tag{23}$$

Ammonia and ammoniacal solutions have been used extensively for other zinc minerals. In a study carried out by Ding et al., (2010), Zn extraction from hemimorphite $(Zn_4(Si_2O_7)(OH)_2 \cdot H_2O)$ was aimed considering the effects of ammonia-ammonium ratio, ammonia concentration, temperature and ammonia ions. Highest Zn recovery was observed at ammonia-ammonium ratio of 0.5. Effects of

NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NH_4HCO_3 and NH_4Cl as ammonia ions and according to the results, the most effective one was determined as NH_4Cl. Order of ammonia ions on the basis of effectiveness is $NH_4HCO_3 < NH_4NO_3 < (NH_4)_2SO_4 < (NH_4)_2CO_3 < NH_4Cl$. Also with the increase in temperature and NH_4Cl concentration, extraction rate of zinc was increased visible. Li et al., (2013) also conducted a study to investigate the solubility of hemimorphite in ammonium sulfate solution $((NH_4)_2SO_4)$. All the experiments were conducted at 25 ºC with 6 g of samples. Solubility of zinc increased from 4.53 mmol/kg to 11.50 mmol/kg with an increase in ammonium sulfate concentration from 0.55 mol/kg to 3.70 mol/kg.

Liu et al., (2012) studied with willemite (Zn_2SiO_4) containing 52.28% Zn. The test sample was produced from roasting of hemimorphite and the study was conducted to investigate the dissolution kinetics of willemite in $(NH_4)_2SO_4-NH_3-H_2O$ system. Since dissolution of silica is rather low in $(NH_4)_2SO_4-NH_3-H_2O$ system and formation of silica gel, leaching rate of willemite was low. But increasing in temperature, solid/liquid ratio and ammonia concentration resulted in an increase in extraction rate.

A study was conducted with an ore containing 29.44% ZnO by Xu et al., (2010) to recover zinc with sulfuric acid (H_2SO_4) leaching under pressure (Equation 24). Within the scope of the study, effects of particle size, sulfuric acid concentration, leaching time, solid/liquid ratio and pressure were examined. Optimum conditions were determined as 98 µm particle size, 0.44 mol/L sulfuric acid concentration, 120 minutes at 140 ºC and 1.4 MPa pressure. With the optimum conditions, 97% Zn extraction was achieved.

$$Zn_4Si_2O_7(OH)_2.H_2O + 4H_2SO_4 \leftrightarrow 4ZnSO_4 + SiO(OH)_6 + 3H_2O \qquad (24)$$
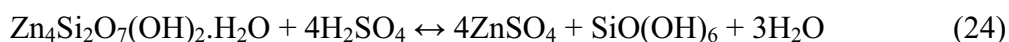
With the light of these studies, enrichment of Kayseri-Develi ore by flotation and ammonia leaching was decided to be studied.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

In this study a carbonate hosted ore containing lead and zinc minerals provided from Kayseri–Develi region of Turkey was used. Kayseri-Develi region mainly consists of oxide minerals such as cerussite ($PbCO_3$), smithsonite ($ZnCO_3$), hydrozincite ($Zn_5(CO_3)_2(OH)_6$), limonite ($Fe(OH)_3$), azurite ($Cu_3(CO_3)_2(OH)_2$) etc. Sulfide type minerals like galena (PbS), sphalerite (ZnS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$) are also seen in the region but, the amount of sulfides are quite a little compared to oxide types. Calcite ($CaCO_3$), clay minerals and dolomite ($CaMg(CO_3)_2$) are also exist in the area as main gangue minerals (Ayhan, 1983). Detailed characteristics of the ore are given in the following sections.

3.2 Method

The study mainly includes determining optimum flotation conditions for a carbonate hosted lead mineral, cerussite ($PbCO_3$), through a set of conventional flotation experiments, and determination of optimum leaching conditions for a zinc oxide mineral, smithsonite ($ZnCO_3$) by ammonia (NH_3) leaching experiments. The main stages in the study are as follows:

i. Physical, chemical, mineralogical and thermal characterization of the ore by various analytical methods involving; Atomic Absorption Spectroscopy (AAS), X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and

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Thermogravimetric analysis (TG/DTG) and Differential Scanning Calorimetry (DSC).

ii. Grindability tests to determine the liberation degree of the ore sample.

iii. Flotation tests. Assessed flotation parameters are;

    a) pH

    b) Amount and conditioning time of sulfidizer,

    c) Collector types and dosages,

    d) Desliming.

iv. Leaching tests to extract zinc from carbonate hosted zinc mineral, smithsonite. Examined conditions during leaching are;

    a) Concentrations of ammonia (NH_3), ammonium chloride (NH_4Cl) and ammonium carbonate ((NH_4)$_2CO_3$),

    b) Leaching time for each concentration of each reagent.

3.3   Experiments

3.3.1   Characterization Studies

Mineralogical analysis, using thin section polarizing microscopy, showed that smithsonite and cerussite are the major minerals in the ore (Figure 3.1). Sphalerite, galena, limonite and pyrite were also seen as minor constituents.
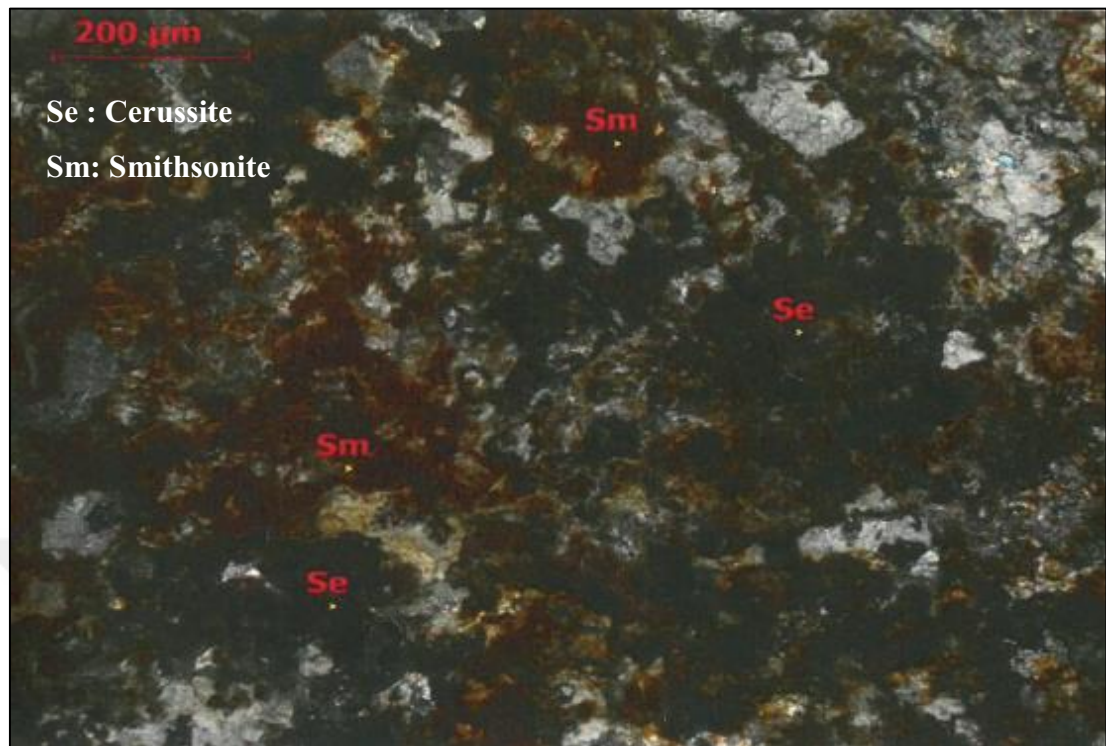
Figure 3.1 Polarized microscopy image of the ore sample

Entities with yellow-red-brown tones are Zn-carbonate (smithsonite) and black entities are Pb-carbonate (cerussite) (Figure 3.1).
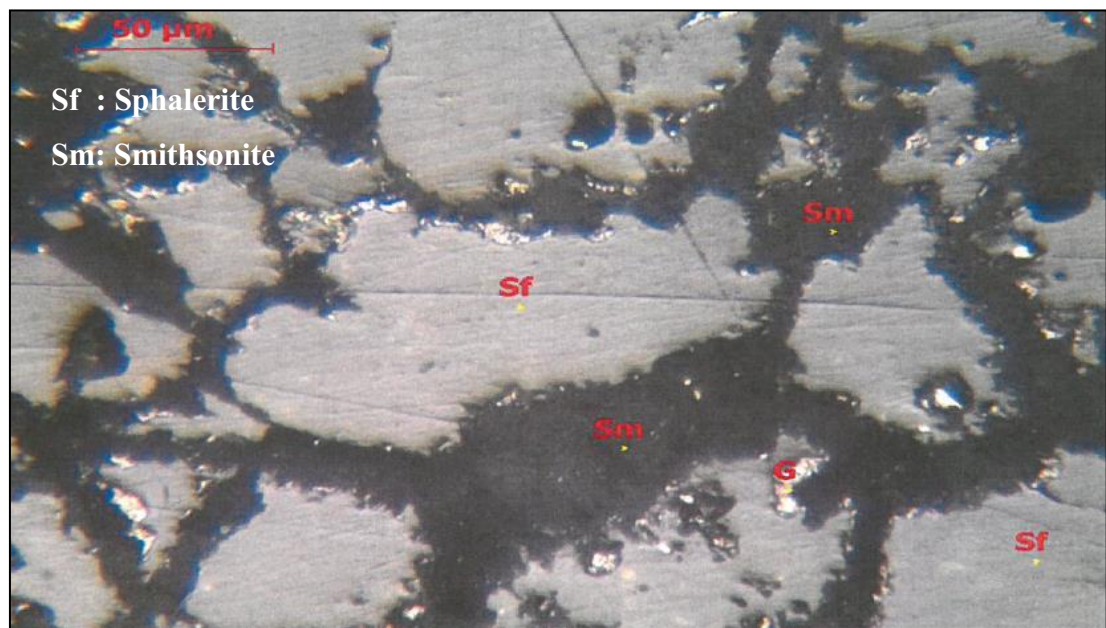
Figure 3.2 Microscopic image of the polished section of sphalerite and smithsonite
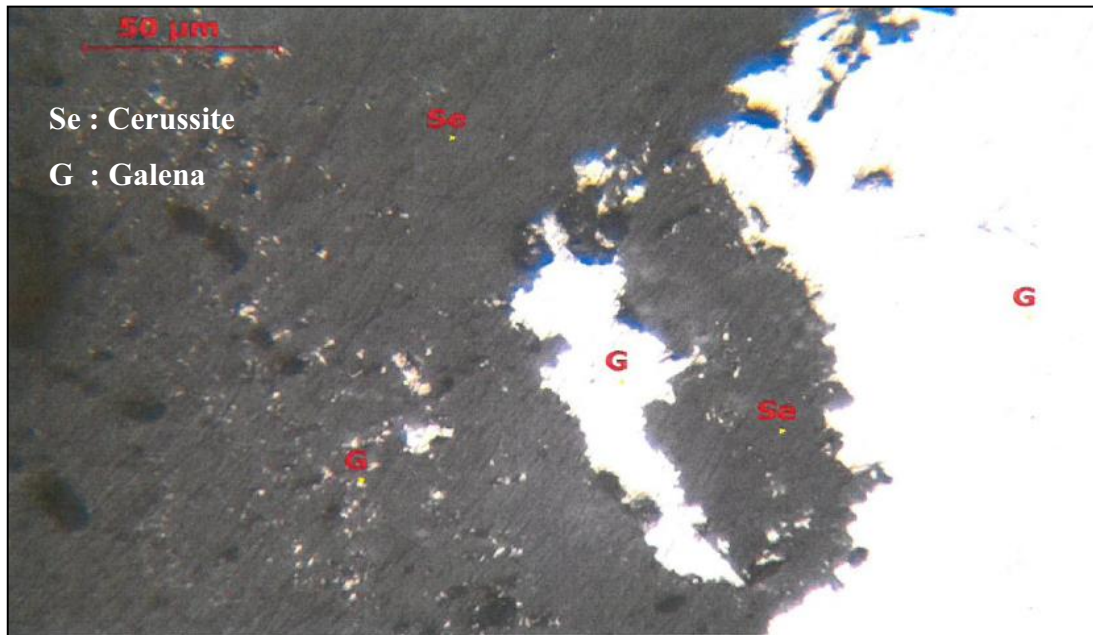
Figure 3.3 Microscopic image of the polished section of galena and cerussite

Sphalerite particles are seen in Figure 3.2 as the lighter shade parts and their edges are observed to be transforming into smithsonite. In
Figure 3.3 3.3, galena particles can be seen, morphing into cerussite particles.

Elemental, mineralogical and chemical analyses of the run-of-mine ore were done using X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Atomic Absorption Spectroscopy (AAS) instruments.

The chemical analysis result of the test sample was carried out with Spectro IQ XRF and the results are given in the Appendix (Table A.1). Develi ore is a potential Pb – Zn resource with 13.59% Pb and 28.31% Zn grades.

Metal distribution of the test sample is determined using Atomic Absorption Spectrometer (AAS) and the results are presented in Table 3.1. Metal distribution of the ore shows that the lead grade is increasing with decreasing particle size (until -

210+150 μm fraction). On the other hand zinc grade is decreasing with decreasing particle size.

Table 3.1 Metal distribution of the test sample

Part. Size (μm)	Weight (%)	Ag (ppm)	Pb (%)	Zn (%)
+1168	27.76	93.00	12.40	30.00
-1168+600	23.98	95.90	13.45	29.60
-600+417	5.42	93.10	14.60	28.10
-417+295	4.24	91.80	15.50	27.90
-295+210	7.03	93.00	16.60	27.70
-210+150	2.37	88.60	17.15	26.60
-150+106	5.02	79.30	15.05	24.70
-106+74	4.10	75.90	15.95	25.70
-74	20.08	57.10	11.0	24.20
		84.95	**13.31**	**27.86**

Figure 3.4 shows the XRD pattern of the run-of-mine ore conducted with Bruker D8 Advance. The ore consists of mainly cerussite (dark blue peaks) and smithsonite (red peaks). The XRD pattern also reveals the presence of hemimorphite $(Zn_4(Si_2O_7)(OH)_2)$ as a secondary zinc mineral in the ore (green peaks). Dolomite detected as gangue mineral (pink peaks). Galena was not observed in XRD pattern because the amount of galena in the ore is very little.
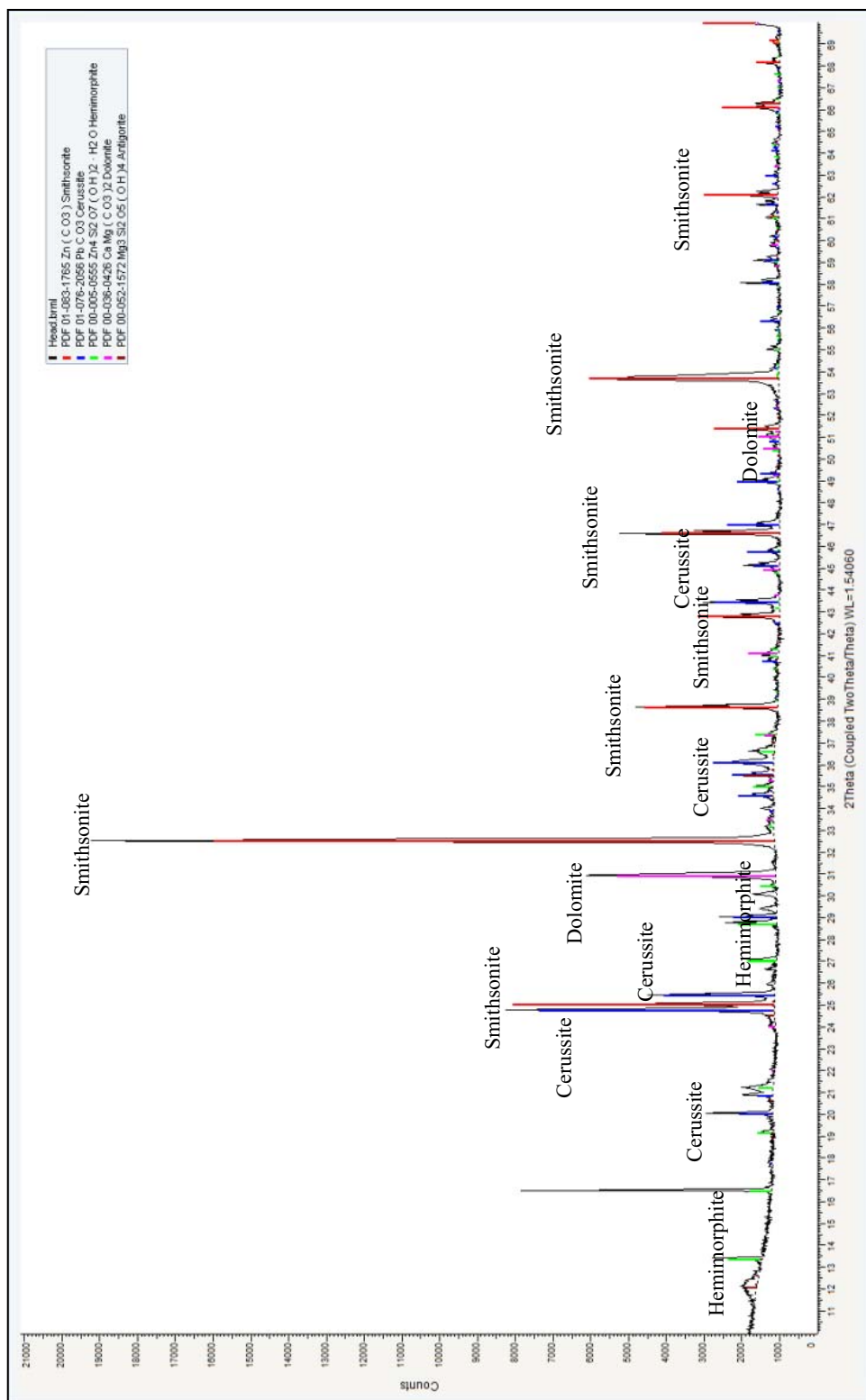
Figure 3.4 X-ray diffraction pattern of the test sample

Thermal characterization of the ore was determined using Thermogravimetric / Differential Thermogravimetry (TG/DTG) and Differential Scanning Calorimetry (DSC) techniques. TG Q500 and DSC Q200 instruments were used for this purpose. TG/DTG measures the weight loss of sample with respect to temperature change. On the other hand, DSC gives information about whether the ore is endothermic and/or exothermic according to the energy change expressed as heat flow. Both TG/DTG and DSC were carried out in pyrolysis mode to observe changes exclusively due to the temperature change from ambient to 600 °C at a 10 °C/min controlled heating rate. During pyrolysis mode, an inert gas (N_2) was supplied to the system. Thermal behavior of the ore can be seen in Figure 3.5 and Figure 3.6.
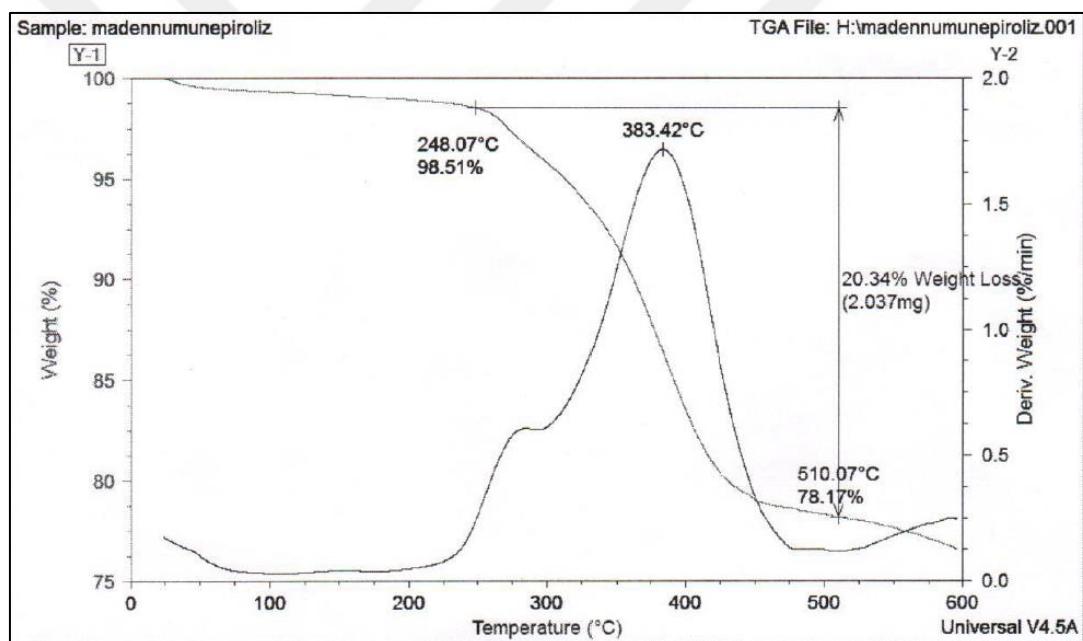
Figure 3.5 TG/DTG profile of Kayseri-Develi ore
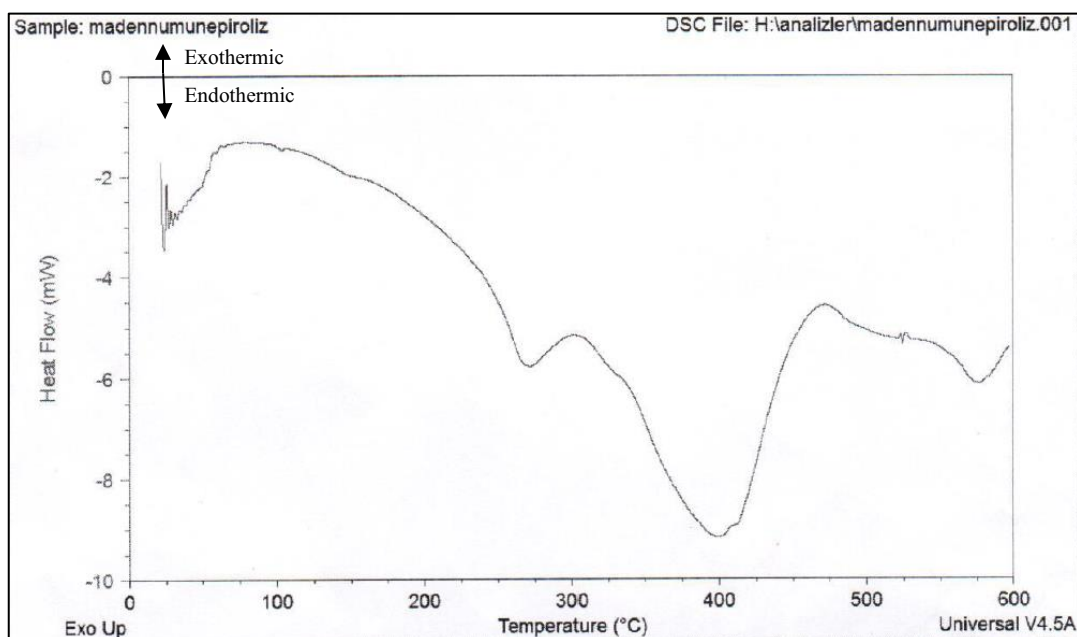
Figure 3.6 DSC profile of Kayseri-Develi ore

From the TG/DTG profile of the ore (Figure 3.5), it was seen that decomposition starts at approximately 250°C and continues until around 510°C. At around 383 °C, there is a sharp weight loss peak due to the decomposition of carbonates (CO_3) to carbon dioxide (CO_2) which also proves that ore is rich in terms of CO_3. After this temperature decomposition still continues but tends to slow down. As a result of TG/DTG profile, more than 20% weight loss occurs due to calcination reactions. The DSC profile of the ore shows that (Figure 3.6), the sample has entirely endothermic behavior because negative heat flow has been recorded through the entire reaction range.

3.3.2 Particle Size Distribution and Grinding Tests

Total sample delivered for this study was 56 kg and around 48 kg of them was used throughout the study. The remaining 8 kg, was kept as arbitration sample. Firstly, 48 kg sample was dry screened using a 2 mm sieve. + 2 mm particles were crushed in a roller crusher and screened again. When 100% of run-of-mine was - 2 mm, it was

wet-screened through a series of sieve of 1168 μm, 600 μm, 417 μm, 295 μm, 210 μm, 150 μm, 106 μm and 74 μm. Particle size analysis showed P_{80} of the ore was 1300 μm. The particle size distribution of the roll-crushed run-of mine ore is presented in the Appendix (Table A.2) and Figure 3.7.
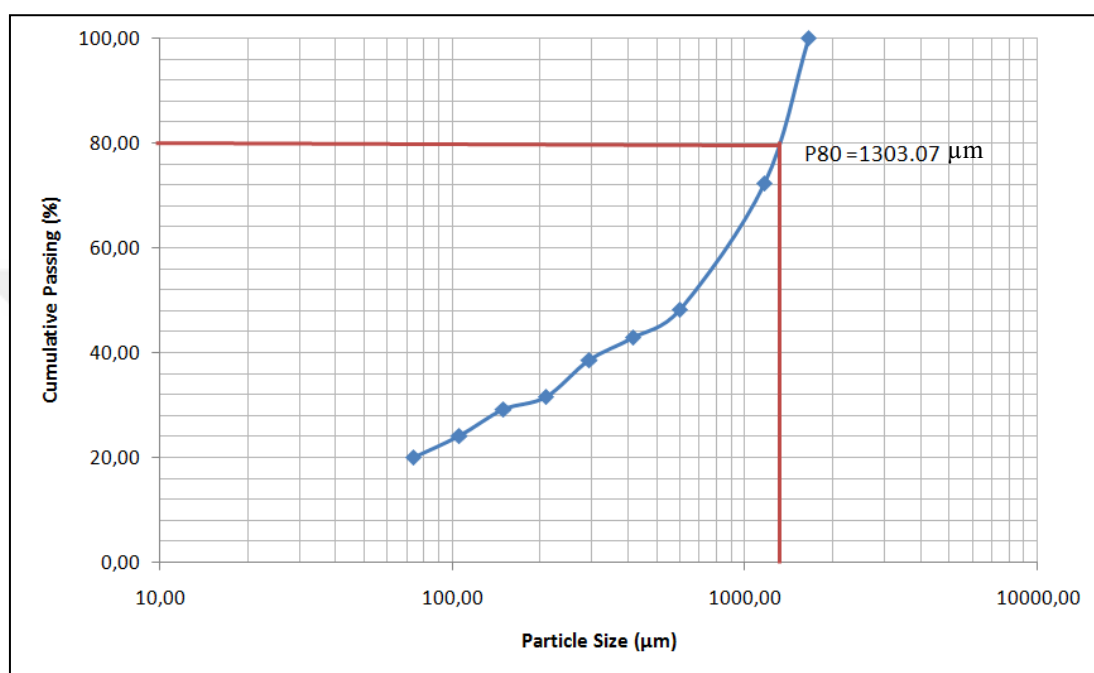
Figure 3.7 Particle size distribution of the run-of mine ore

To achieve required liberation for flotation, wet grinding was applied for 5, 10, and 15 minutes using a laboratory scale rod mill. The rod mill has 32.5 cm length, 19.5 cm inner diameter and 22 cm outer diameter. Its rotational speed was kept at 44 rpm. As the mill charge, four 2.54 cm (1 inch) and eight 1.905 cm (3/4 inch) rods were used and the pulp density was adjusted to 50% solids by weight.

After grinding, sieve analysis was performed. The post-grinding particle size distributions with respect to different grinding periods are presented in the Appendix (Table A.3). Graphical representation of the particle size distribution after 5, 10, and 15 minutes of grinding is also given in Figure 3.8.
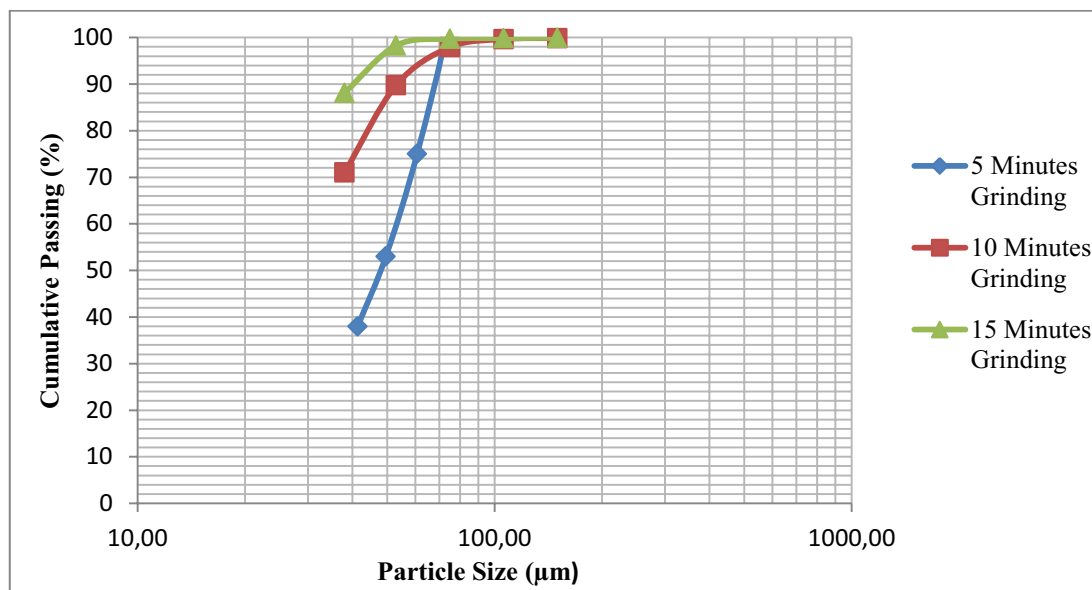
Figure 3.8 Grindability test results with different grinding periods

According to the results, 10 minutes of grinding was decided to be sufficient with more than 97% of the material is -75 μm.

3.4 Flotation of Lead Minerals

For flotation tests, Denver laboratory type flotation machine with a 1 liter cell was used. For the tests impeller speed was adjusted to 1045 rpm. Flotation tests were carried out with approximately 375 g material and approximately 30% by weight pulp density. The experimental setup is shown below (Figure 3.9).

Figure 3.9 Experimental setup of flotation tests

Prior to galena and cerussite flotation experiments, effect of pH was investigated. Pulp was initially conditioned with sodium hydrosulfur (NaHS) for sulfidization, then, adjustment of pH was achieved using sodium carbonate (Na_2CO_3, Merck). Lime was not chosen due to its depression effect on galena. Experiments were conducted starting from natural pH (around 7.5) of the ore to 10.5 by 0.5 increments. As a result of the experiments, pH 9.5 was determined as the optimum condition. In Table 3.2, examined pH values are seen.

Table 3.2 Examined pH values

Experiment No.	pH
1	Natural (7.5)
2	8.5
3	9.0
4	9.5
5	10.0
6	10.5

Other constant parameters during pH tests are listed below;

- Dosage and conditioning time of sulfidizer (NaHS): 1000 g/t, 10 min.
- Dosage and conditioning time of collector potassium amyl xanthate (KAX): 200 g/t, 10 min.
- Dosage of frother methyl isobuthyl carbinol (MIBC): 80 g/t
- Flotation time: 5 min.
- Impeller speed: ~ 1045 rpm

The recovery results obtained from pH adjustment tests were very low, thus two more tests were carried out using 2000 g/t and 3000 g/t NaHS in order to determine the cause of low recovery results. Since these additional experiments did not yield any improvement, rest of the study was conducted using Na_2S as sulfidizer. Also instead of MIBC, Cytec F-533 was decided to be used as frother since low froth zone was observed.

Several flowsheets including cleaner stages and desliming stage were tried and as a result of the chemical analysis conducted by Shimadzu A-7000 model AAS, flowsheet in Figure 3.10 was decided to be followed for the rest of the experiments since that sufficient grade and recovery values were obtained with this flowsheet.
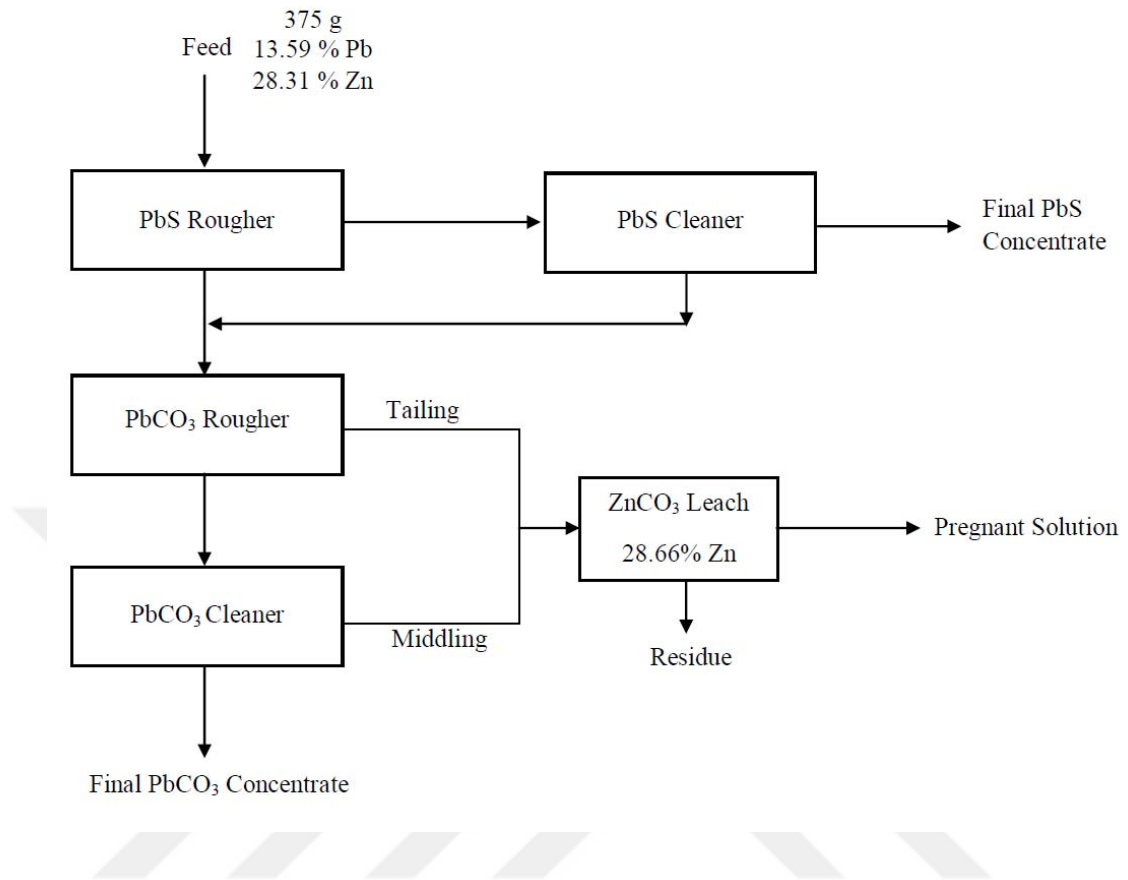
Figure 3.10 Flowsheet followed through the flotation tests

3.4.1 Galena (PbS) Flotation

Even though trace amount of galena is present in the ore since the experiments conducted for obtaining Pb from galena gave good results, galena flotation was decided prior to cerussite flotation. Two-stage flotation was applied and effects of collector type and dosage were examined for the flotation of galena.

3.4.1.1 Effect of Collector Type

As it is known galena can be floated using sulphydryl type collectors. For flotation of galena, effects of potassium amyl xanthate (KAX), potassium ethyl xanthate (KEX), sodium isopropyl xanthate (SIPX), Aerophine 3418A (modified dithiophosphate) and mixture of KAX+Aerophine 3418A were investigated (Table 3.3).

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Table 3.3 Collectors used for flotation of galena

Experiment No.	Collectors
7	KAX
8	KEX
9	SIPX
10	Aerophine 3418A
11	Aerophine 3418A + KAX

Other parameters that were kept constant while performing these experiments are given below;

- pH : ~ 9.5
- Dosage and conditioning time of the collectors for galena: 200 g/t
- Dosage and conditioning time of KAX for cerussite: 400 g/t
- Dosage and conditioning time of Na_2S for cerussite: 2000 g/t
- Dosage of frother F-533: 53 g/t
- Flotation time: 5 min.
- Cleaning time: 5 min.
- Impeller speed: ~ 1045 rpm

3.4.1.2 Effect of Collector Dosage

Since galena is a mineral with sulphur in its structure, it can be floated easily with less amount of collector compared to minerals without sulphur in their structure. For flotation of galena, effect of collector dosage was examined using potassium amyl xanthate (KAX) for 100 and 200 g/t (Table 3.4).

Table 3.4 Collector dosages examined for flotation of galena

Experiment No.	Collector	Collector Dosage (g/t)
12	KAX	100
13	KAX	200

Other parameters that were kept constant during these experiments are given below;

- pH : ~ 9.5
- Dosage and conditioning time of KAX for cerussite: 400 g/t, 10 min.
- Dosage and conditioning time of Na_2S for cerussite: 2000 g/t, 10 min.
- Dosage of frother F-533: 53 g/t
- Flotation time: 5 min.
- Cleaning time: 5 min.
- Impeller speed: ~ 1045 rpm

3.4.2 Cerussite ($PbCO_3$) Flotation

In order to optimize flotation conditions for cerussite, tests at varying conditions of sulfidizing agent, collectors and desliming were performed. At the end of each test, products were dried in a laboratory furnace, weighted and prepared for assaying.

3.4.2.1 Effect of Sulfidizing Agent

To float oxide minerals, the most frequently used method is converting an oxide surface into a sulfurous surface (Li et al., 2010). Analytical grade sodium sulfide (Na_2S-Merck) was used as 1% by weight solution to determine the optimum amount of sulfidizing agent. Na_2S was then tested for optimum dosage and conditioning time. Three different dosages of 1000, 1500 and 2000 g/t were tested separately for 10, 15 and 20 minutes of conditioning time. For all experiments, pH was adjusted to around 9.5, 400 g/t potassium amyl xanthate (KAX) was used as collector and 53 g/t Cytec F-533 (mixture of alcohols, esters and glycols) was used as frother. The parameters examined are listed in Table 3.5.

Table 3.5 Examined sulfidizer (Na$_2$S) parameters

Experiment No.	Amount of Na$_2$S (g/t)	Conditioning Time for Na$_2$S (min.)
14	1000	10
15	1000	15
16	1000	20
17	1500	10
18	1500	15
19	1500	20
20	2000	10
21	2000	15
22	2000	20

Other parameters that were kept unchanged for this set of test are listed below;

- pH : ~ 9.5
- Dosage and conditioning time of KAX for galena: 200 g/t, 10 min.
- Dosage and conditioning time of KAX for cerussite: 400 g/t, 10 min.
- Dosage of frother F-533: 53 g/t
- Flotation time: 5 min.
- Cleaning time: 5 min.
- Impeller speed: ~ 1045 rpm

3.4.2.2 Effect of Collector Type

Several tests were conducted to observe the effect of different collectors on cerussite flotation. For flotation of cerussite, KAX, KEX, SIPX, Aerophine 3418A and also mixtures of KAX+Aero 404 (dithiophosphate salt in water) and KAX+Aero 407 (dithiophosphate and mercapto benzo thiazole salts in water) were tested. In all tests, the dosages of collectors kept constant as 400 g/t. Conditioning time after addition of

collectors was determined as 10 minutes. The experimental conditions for assessing the effect of collectors are presented in Table 3.6.

Table 3.6 Collectors used for flotation of cerussite

Experiment No.	Collectors
23	KAX
24	KEX
25	SIPX
26	Aerophine 3418A
27	Aero 404+KAX
28	Aero 407+KAX

Operational conditions are listed below;

- pH : ~ 9.5
- Dosage and conditioning time of KAX for galena: 200 g/t, 10 min.
- Dosage and conditioning time of collectors for cerussite: 400 g/t, 10 min.
- Dosage and conditioning time of Na_2S for cerussite: 2000 g/t, 10 min.
- Dosage of frother F-533: 53 g/t
- Flotation time: 5 min.
- Cleaning time: 5 min.
- Impeller speed: ~ 1045 rpm

3.4.2.3 Effect of Collector Dosage

To observe the effect of collector dosage on cerussite flotation, KAX was used for 300 and 400 g/t (Table 3.7).

Table 3.7 Collector dosages examined for flotation of cerussite

Experiment No.	Collector	Dosage of Collector
29	KAX	300
30	KAX	400

Operational conditions are listed below;

- pH : ~ 9.5
- Dosage and conditioning time of KAX for galena: 200 g/t, 10 min.
- Dosage and conditioning time of Na_2S for cerussite: 2000 g/t, 10 min.
- Dosage of frother F-533: 53 g/t
- Flotation time: 5 min.
- Cleaning time: 5 min.
- Impeller speed: ~ 1045 rpm

3.4.3 Effect of Desliming

It is well known that slimes have negative impacts on flotation of oxidized minerals. For this purpose effect of desliming in advance of lead flotation was studied. In this regard, two tests were performed. Prior to one of the tests 375 g sample was screened from 38 μm sieve and second test was conducted using 20 μm sieve. Operational data for these tests is listed below;

- pH : ~ 9.5
- Dosage and conditioning time of KAX for galena: 200 g/t, 10 min.
- Dosage and conditioning time of KAX for cerussite: 400 g/t, 10 min.
- Dosage and conditioning time of sulfidizer (Na_2S): 2000 g/t, 10 min.
- Dosage of frother F-533: 53 g/t
- Flotation time: 5 min.
- Cleaning time: 5 min.
- Impeller speed: ~ 1043 rpm

3.5 Ammonia Leaching of Smithsonite ($ZnCO_3$)

Due to the fact that enrichment of smithsonite using conventional flotation technique was not achieved successfully, leaching was selected for this study. Within this

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context, leaching of smithsonite using agitated ammonia leaching was attempted. The feed material for leaching was the tailing of cerussite flotation which contains 28.66% Zn. The XRD pattern of the leach feed is presented in Figure 3.11. It is seen that cerussite peaks disappeared following the flotation tests. However, smithsonite, hemimorphite, dolomite were not affected by flotation.

In all the leaching tests, 400 ml beakers were used at ambient temperature (25℃) and solid/liquid ratio was taken as 1:10 based on other studies (Ju et al., 2005; Wang et al., 2008). In the leaching tests, effect of leaching reagent and reagent concentration and effect of leaching time were investigated.

Figure 3.11 XRD pattern of the leach feed

3.5.1 Effect of Leaching Reagent, Reagent Concentration and Leaching Time

To observe the effects of leaching reagent and reagent concentration, ammonia (NH_3), ammonium chloride (NH_4Cl) and ammonium carbonate ((NH_4)$_2CO_3$) were used. 5 M and 7 M reagent solutions were prepared in 500 ml volumetric flasks and leaching was conducted for 30 minutes, 1 hour, 3 hours, 6 hours and 12 hours. At the end of the tests, solutions in the beakers were filtered and residues were dried, weighted and prepared for assaying. Chemical analysis procedures of lead and zinc are provided in the Appendix. In Table 3.8, examined parameters for the leaching tests are shown.

Table 3.8 Parameters examined during leaching tests

Experiment No.	Leaching Reagent	Concentration of the Reagent (M)	Conditioning Time (min.)
1	NH_3	5	30, 60, 180, 360, 720
2	NH_3	7	30, 60, 180, 360, 720
3	NH_4Cl	5	30, 60, 180, 360, 720
4	NH_4Cl	7	30, 60, 180, 360, 720
5	$(NH_4)_2CO_3$	5	30, 60, 180, 360, 720
6	$(NH_4)_2CO_3$	7	30, 60, 180, 360, 720

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Flotation of Lead Minerals

4.1.1 Galena Flotation

Two-stage flotation (rougher+cleaner) was decided according to a preliminary experiment comparing one and two stage of flotation. The concentrate obtained from one-stage flotation was contained 45.12% Pb with 10.04% recovery. On the other hand, adding cleaner stage increased the Pb grade and recovery considerably.

4.1.1.1 Effect of Collector Type

The results obtained from the experiments are presented in the Appendix (Table A.4) and Figure 4.1, respectively.

Potassium amyl xanthate (KAX) was chosen as optimum collector for galena flotation since the experiment conducted with KAX was more satisfactory compared to others. By using KAX, a galena concentrate containing 75.81% Pb with 7.23% recovery was obtained.

Although the experiments performed with SIPX and mixture of Aerophine 3418A and KAX were promising, still, KAX is better in terms of grade and recovery. The experiments carried out with KEX and Aerophine 3418A resulted with very low grade and recovery values.
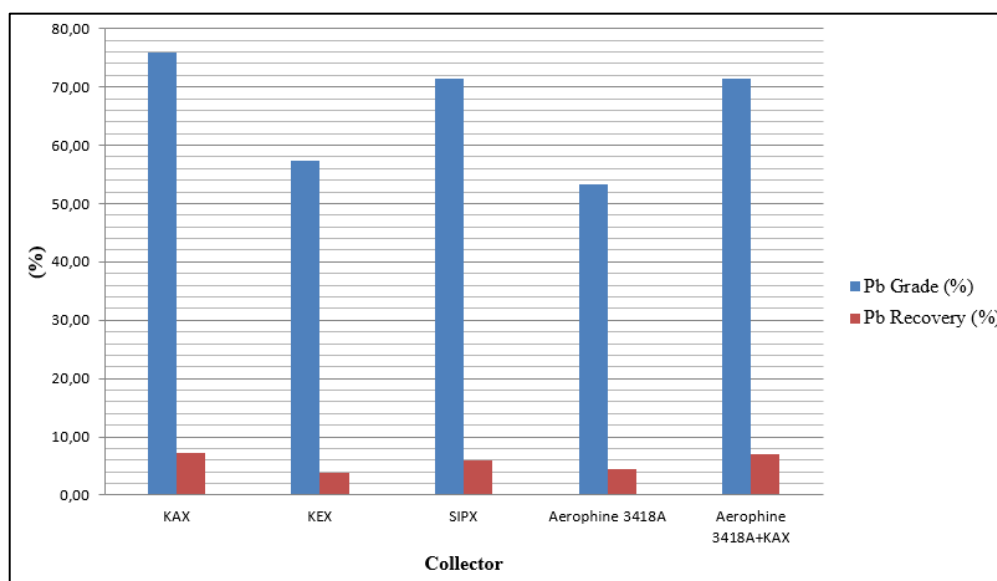
Figure 4.1 Effect of collector type on Pb grade and recovery in galena concentrate

4.1.1.2 Effect of Collector Dosage

The results of the experiments conducted to examine the effect of collector dosage on galena are given in the Appendix (Table A.5) and Figure 4.2. 100 and 200 g/t of KAX was used and 200 g/t KAX gave better result compared to half of that dosage. Rest of the study was continued using 200 g/t KAX for flotation of galena.
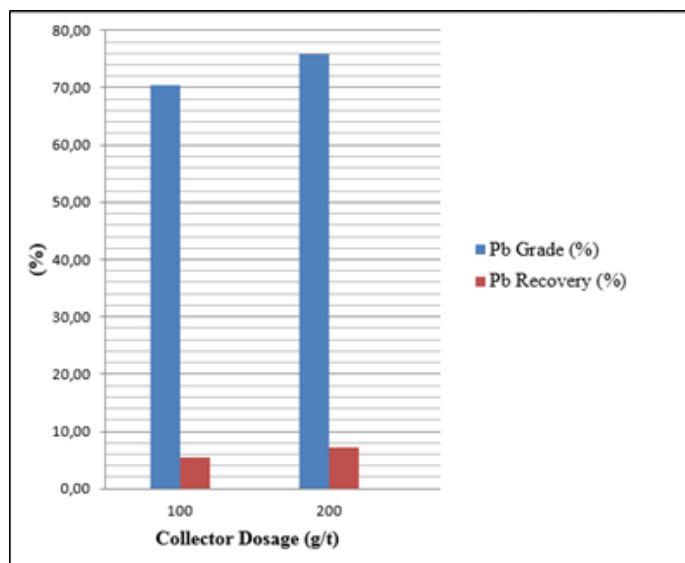
Figure 4.2 Effect of collector dosage on Pb grade and recovery in galena concentrate

4.1.2 Cerussite Flotation

For cerussite flotation two stages of flotation (rougher+cleaner) was decided according to a preliminary experiment comparing one and two-stage of flotation similar to flotation of galena. With one-stage of flotation a concentrate with 57.5% Pb with 75% recovery was produced. As for two stage of flotation Pb grade increased reasonably.

4.1.2.1 Effect of Sulfidizing Agent

A series of tests were carried out to determine the optimum dosage and also conditioning time for sulfidizing agent. The results are seen in the Appendix (Table A.6) and Figure 4.3.
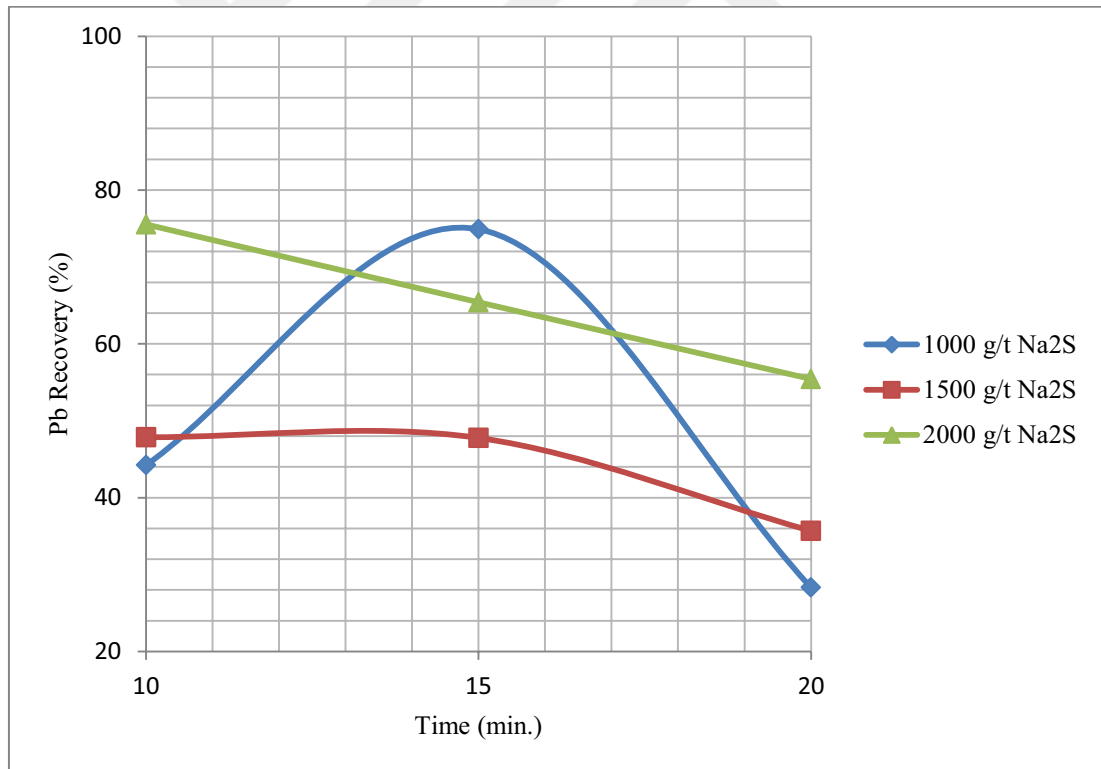
Figure 4.3 Effect of dosage and conditioning time of Na_2S on Pb recovery in cerussite concentrate

Optimum dosage for sulfidizing agent was determined as 2000 g/t with 10 minutes conditioning. It is observed that increasing conditioning time after 15 minutes has a negative effect on recovery for every Na_2S dosages. Since both grade and recovery results are satisfactory and economically viable, 2000 g/t Na_2S with 10 minutes of conditioning was selected as optimum flotation parameters for this ore.

4.1.2.2   Effect of Collector Type

The results obtained from the experiments are presented in the Appendix (Table A.7). Also graphical representation is seen in Figure 4.4.
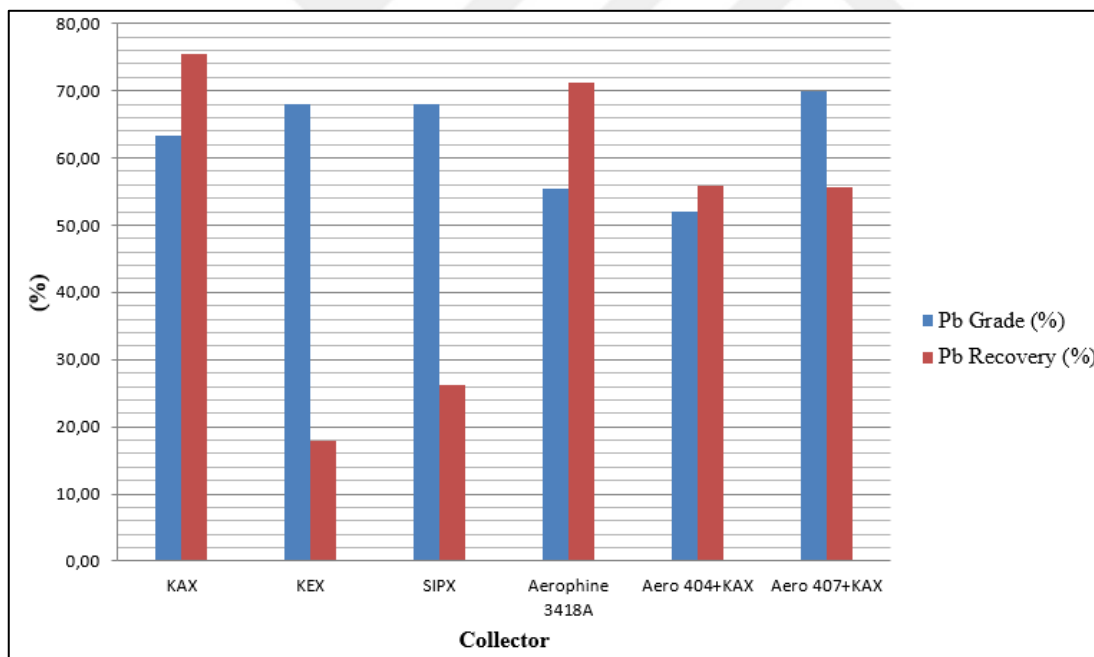
 Figure 4.4 Effect of collector type on Pb grade and recovery in cerussite concentrate

At the end of the experiments carried out to investigate the effect of collector type, a cerussite concentrate containing 63.25% Pb with 75.53% recovery was achieved.

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KAX was chosen as optimum collector because grade and recovery results obtained by KAX are more satisfactory. Using other collectors given in **Error! Reference ource not found.** caused very sharp decrease in recovery and slight fluctuation in grade. Even though Pb grade of experiment performed using mixture of Aero 407+KAX is the highest among others, recovery of this experiment is rather low.

4.1.2.3 Effect of Collector Dosage

300 and 400 g/t of KAX was used to observe the effect of collector dosage and results are presented in the Appendix (Table A.8) and Figure 4.5. In terms of Pb grade, 300 and 400 g/t KAX gave close results but in terms of recovery, the difference between two dosages are considerably high. And since both Pb grade and recovery of the test result obtained using 400 g/t KAX is more satisfactory, 400 g/t of KAX was used for the rest of the study.
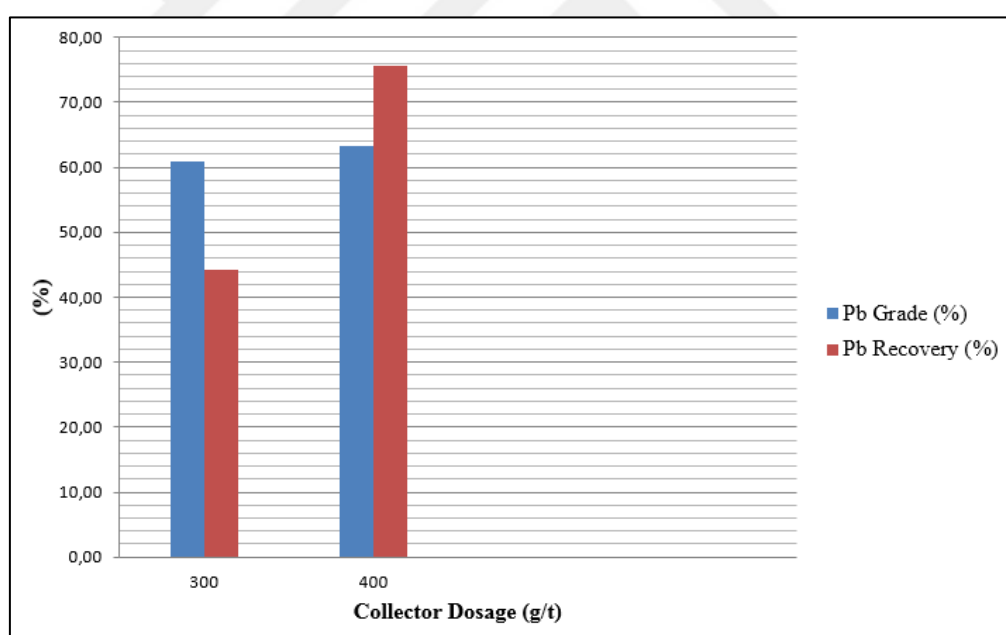
Figure 4.5 Effect of collector dosage on Pb grade and recovery in cerussite flotation

4.1.3 Effect of Desliming

Desliming tests were conducted using 20 and 38 µm sized sieves. Flotation tests were performed with +38 µm and +20 µm sized particles.

Recovery of Pb in galena concentrate decreased dramatically with the removal of -38 µm. In addition, galena concentrate could not be obtained following the removal of -20 µm sized particles. Even though the lead grade in cerussite flotation increases, since galena concentrate could not be obtained, desliming with 20 µm was not preferred. Also lead grade increases sharply in middling in a negative way. Experimental results are given in Table 4.1 and Table 4.2 respectively.

Table 4.1 Effect of desliming on Pb grade and recovery using 38 µm sieve

Pb (%) in Galena Conc.	Pb (%) in Cerussite Conc.	Pb (%) in Middling	Pb (%) in Slime	Pb (%) in Tailing	Total Pb Rec. (%)
32.88	63.80	2.25	13.45	1.19	45.95

Table 4.2 Effect of desliming on Pb grade and recovery using 20 µm sieve

Pb (%) in Cerussite Conc.	Pb (%) in Middling	Pb (%) in Slime	Pb (%) in Tailing	Total Pb Rec. (%)
67.96	12.51	13.36	1.85	49.80

The chemical analyses to determine Pb grade were also applied to middlings and tailings. Additionally, Zn grade in each component of flotation were assessed. These results are presented in the Appendix (Table A.9 and Table A.10).

4.2 Additional Flotation Tests

For the purpose of improving flotation efficiency, some additional experiments were carried out.

In order to decrease Zn content in galena concentrate, 400 g/t (zinc sulfate) $ZnSO_4$ was added and conditioned for 5 minutes. Since there was not any apparent improvement in Zn content, it was decided not to be used. The result is given in the Appendix (Table A.11).

Another experiment was conducted in order to see whether adjusting pH prior to cerussite flotation has any effect on Pb grade or recover. As a result of the experiment, it was seen that adjusting pH prior to cerussite flotation has not significant effect on Pb grade or recovery. The result is provided in the Appendix (Table A.12).

Moreover, column flotation of galena and cerussite was conducted. For the experiments, Ünal floatation column with the dimensions of 5.4 cm inner, 6 cm outer diameter and 100 cm height was used (Figure 4.6) under the optimum conditions obtained from conventional flotation cell.

Figure 4.6 Experimental setup of column flotation

The aim was to compare the best results obtained from conventional flotation technique with column flotation. Unfortunately, the experiments conducted by flotation column did not give viable results, especially in terms of froth formation. For that reason, additional tests were not performed on flotation column. The highest Pb grade obtained from galena concentrate was 59.22% and 48.01% from cerussite concentrate. On the other hand, highest recovery was 39.17%.

In addition to flotation of lead minerals, flotation of smithsonite was also studied. For that purpose, effects of dosage (2000, 3000, 4000 g/t) and conditioning time of sulfidizing agent (10, 20, 30 min.), collector type (Alkyle Amine Acetate (Armac C) and Cytec3100) and dosages (200 and 400 g/t), addition of frother and dosage of frother (53 and 27 g/t F-533), desliming and pulp temperature were investigated. The results were not satisfactory and reagent consumption was very high. Only desliming (using 38 μm sieve) gave viable result to decrease Zn grade in tailing. Other tests even with the high amounts of Na_2S addition did not give viable results. So that, ammonia leaching was selected to beneficiate smithsonite.

4.3 Smithsonite Leaching

Effect of ammonia (NH_3), ammonium chloride (NH_4Cl) and ammonium carbonate ((NH_4)$_2CO_3$) at various concentrations and leaching durations on leaching of smithsonite was investigated. 5 and 7 M solutions were prepared from these reagents and the ore was leached for five different time periods: 30 minutes, 1 hour, 3 hours, 6 hours and 12 hours.

The results of the experiments are provided in Table 4.3 and graphical representations of each reagent with respect to time and concentration can be seen in Figure 4.7, Figure 4.8 and Figure 4.9. Extraction of Zn was calculated according to the equation below:

$$\% \text{ Zn Extraction} = \left\{ 100 - \frac{\text{Zn grade (\%)in residue} * \text{Weight of residue}}{\text{Zn grade (\%)in ore} * \text{Weight of ore}} * 100 \right\}$$

Table 4.3 Effect of leaching reagent and reagent concentration on Zn extraction

Leaching Reagent	Concentration (M)	Leaching Time (min.) Zn Extraction (%)				
		30	60	180	360	720
NH$_3$	5	25.79	32.40	59.42	72.77	75.04
NH$_3$	7	35.63	49.75	66.37	74.30	76.66
NH$_4$Cl	5	77.63	81.74	79.76	77.03	77.44
NH$_4$Cl	7	76.75	77.79	78.19	78.16	77.91
(NH$_4$)$_2$CO$_3$	5	79.17	82.37	79.34	81.52	81.53
(NH$_4$)$_2$CO$_3$	7	81.20	79.85	84.19	84.92	85.62
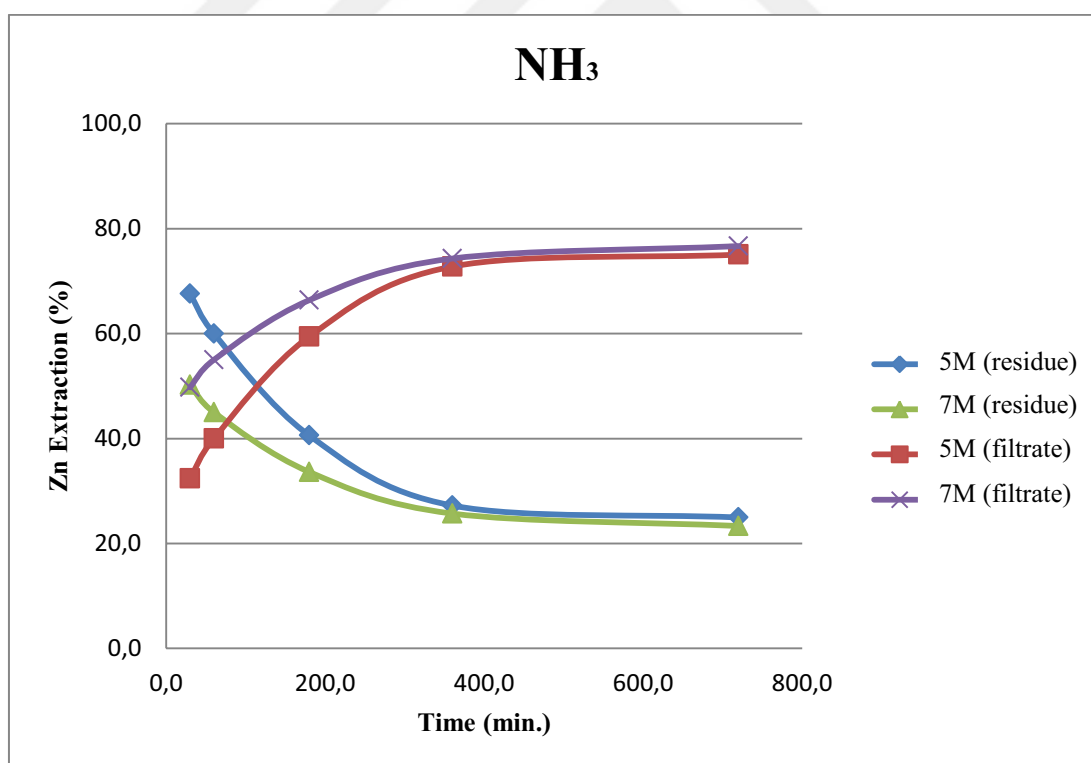
Figure 4.7 Effect of NH$_3$ concentration on Zn extraction
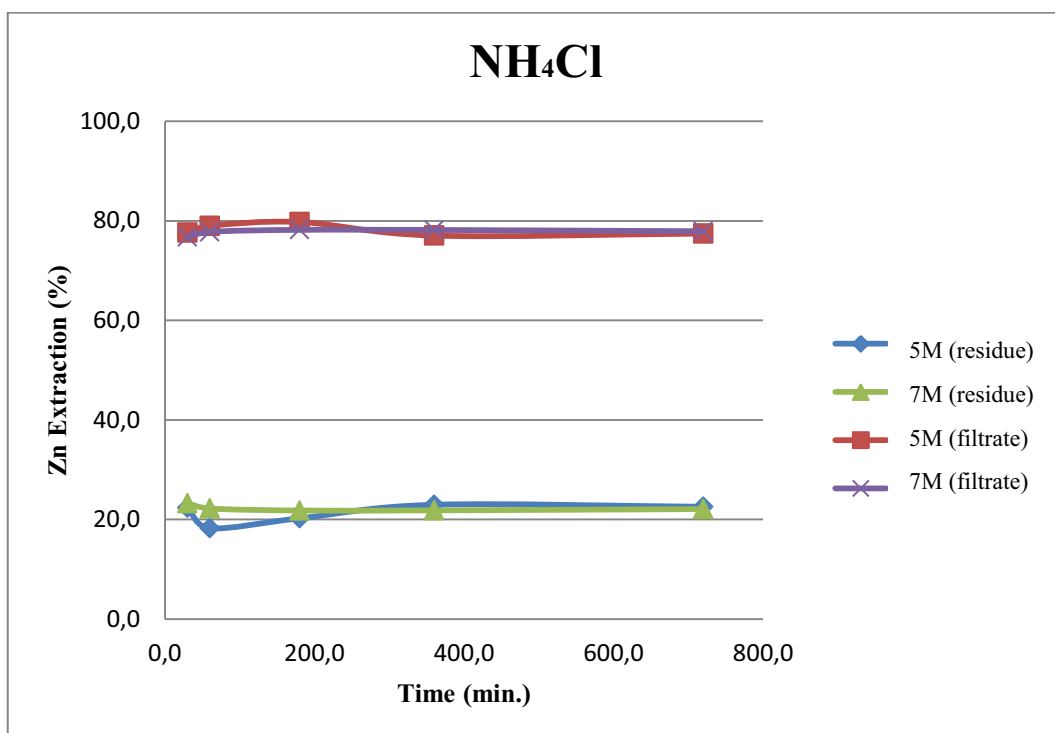
Figure 4.8 Effect of NH₄Cl concentration on Zn extraction
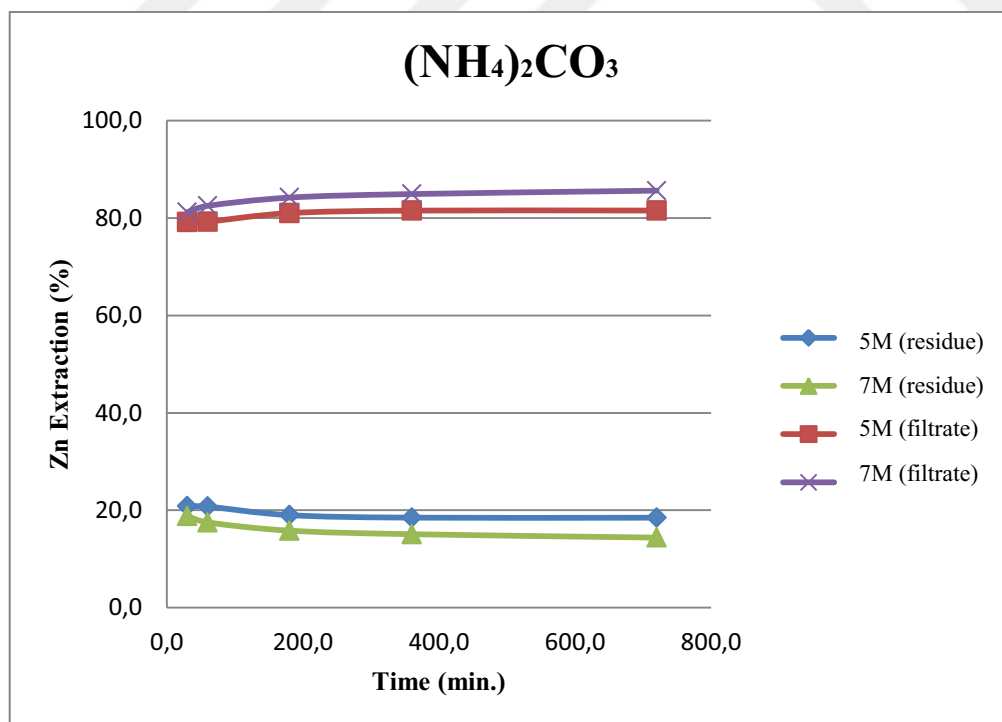
Figure 4.9 Effect of (NH₄)₂CO₃ concentration on Zn extraction

From Table 4.3, it can be concluded that increasing in reagent concentration causes an increase in extraction rate. In addition to that, longer leaching duration gives higher recovery result. Ranking of applied reagents in terms of extraction % is;

$$(NH_4)_2CO_3 > NH_4Cl > NH_3$$
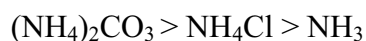
Eventhough the highest recovery (nearly 86 %) was achieved using 7 M of ammonium carbonate ($(NH_4)_2CO_3$) solution with 720 minutes (12 hours) of leaching duration, Zn extraction did not increased in high amounts after 180 minutes of leaching duration with 7 M of ammonium carbonate.

Final flowsheet of the study together with the optimum conditions is presented in Figure 4.10
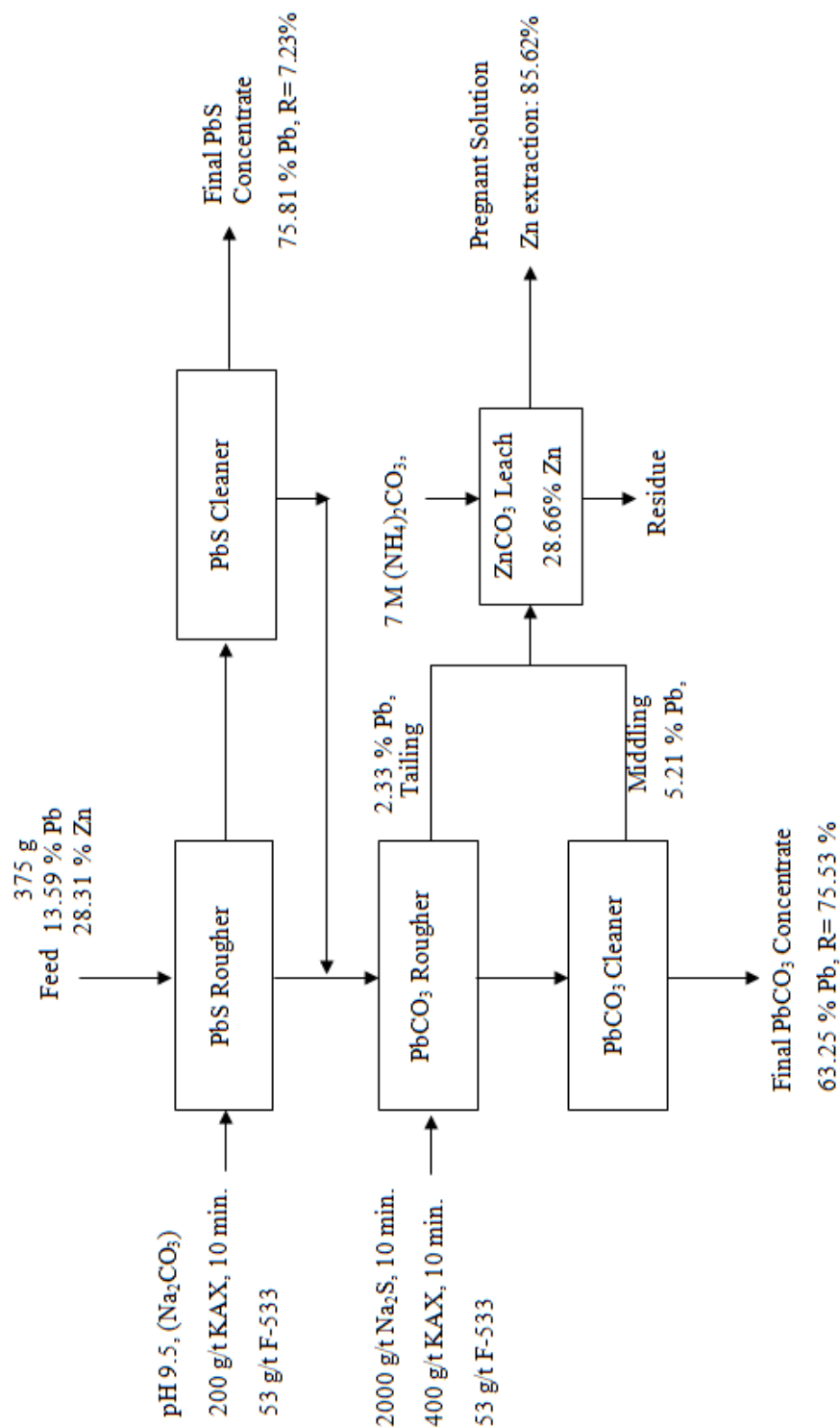
Figure 4.10 Final flowsheet of the study

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

In consequence of flotation and leaching experiments, following conclusions are deducted;

- A galena concentrate having 75.81% Pb with 7.23% recovery was produced using 200 g/t KAX as optimum collector. KEX and Aerophine 3418A were not suggested for galena flotation since that the experiments conducted with these reagents resulted with the lowest values in terms of both grade and recovery.

- A cerussite concentrate containing 63.25% Pb with 75.53% recovery was produced. As a result of the tests, 2000 g/t sodium sulfide (Na_2S) with 10 minutes of conditioning was determined due to its better result compared to other dosages of Na_2S. Among various collectors used, potassium amyl xanthate (KAX) was determined as suitable for cerussite flotation with the dosage of 400 g/t.

- The experiments conducted to observe the effect of desliming resulted that, desliming has negative effect on flotation of lead minerals.

- Smithsonite was also attempted to be enriched by flotation but the results were not promising to continue. Therefore agitating ammonia leaching was decided to be used for smithsonite.

- At the end of the leaching experiments, it was seen that increasing the reagent concentration resulted in increase in the extraction rate of Zn. Reagents gave better results in the order of; $(NH_4)_2CO_3 > NH_4Cl > NH_3$. Also longer leaching duration resulted with more Zn extraction.

- The highest Zn extraction of 86% was succeed with 7 M ammonium carbonate $((NH_4)_2CO_3)$ solution after 12 hours of leaching at ambient temperature (~25℃). But actually, Zn extraction did not increased in high amounts after 180 minutes of leaching duration with 7 M of ammonium carbonate.

In this study, even though many flotation tests were carried out for smithsonite, there were not any successful results. Since there are various studies succeeded in smithsonite flotation, more comprehensive studies should be conducted with new techniques on smithsonite flotation such as flotation without a sulfidizer. Also column flotation of this ore should be studied more thoroughly.

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APPENDIX

Table A.1 Chemical analysis of the test sample

Pb (%)	Zn (%)	Ag (ppm)	Al (%)	Ca (%)	Fe (%)	K (%)	Na (%)	S (%)	Mg (%)	Cu (ppm)	Cr (ppm)	Si (%)	C+O (%)
13.59	28.31	89	0.49	2.57	5.41	0.05	0.01	0.17	0.78	9.4	40	5.28	43.34

Table A.2 Particle size distribution of run-of mine ore

Part. Size (µm)	Weight (%)	Cumulative O/S (%)	Cumulative U/S (%)
+1168	27.76	27.76	72.24
-1168+600	23.98	51.74	48.26
-600+417	5.42	57.16	42.84
-417+295	4.24	61.40	38.60
-295+210	7.03	68.44	31.56
-210+150	2.37	70.80	29.20
-150+106	5.02	75.93	24.17
-106+74	4.10	79.92	20.08
-74	20.08		
	100.00		

Table A.3 Particle size distribution of the ore with different grinding periods

Particle Size	5 Minutes		10 Minutes		15 Minutes	
μm	Weight (%)	Cum. U/S (%)	Weight (%)	Cum. U/S (%)	Weight (%)	Cum. U/S (%)
+150	6.80		0.13		0.07	
-150+106	17.64	93.20	0.21	99.87	0.07	99.93
-106+75	14.90	75.56	1.72	99.66	0.14	99.85
-75+53	11.05	60.65	8.18	97.93	1.43	99.72
-53+38	8.25	49.60	18.74	89.76	10.16	98.28
-38	41.35	41.35	71.02	71.02	88.12	88.12
	100.00		100.00		100.00	

Chemical Analysis Procedures for Lead and Zinc

Chemical analyses were performed using Atomic Absorption Spectrometer.

Chemical analysis steps for lead are follows;

1. Sampling is applied to take 1 g from dried and weighted material for the analysis.

2. 1 g of material is kept in the furnace at 105℃ for approximately an hour to get rid of its moisture. Then it is kept at the desiccators for 15 minutes to let it cool down and also to prevent it from moisture.

3. For lead analysis, 30 ml nitric acid   (HNO_3) is added to 1 g of material and it is allowed to dissolve at 100℃. 50 ml distilled water is added when brown smokes diminishes and the sample is removed from hot plate when it starts to boil.

4. As final step, the solution in the beaker is filtered and filtrate is analyzed in Atomic Absorption Spectrometer (AAS).

Chemical analysis procedure for zinc is as follows;

1. For zinc analysis, 0.1 g of material is sampled,

2. 0.1 g of material is kept in the furnace and then in the desiccators similar to the lead analysis.

3. 30 ml of nitric acid (HNO_3) and 45 ml of hydrochloric acid (HCl) are added to 0.1 g of material and left overnight.

4. Following day, the solution is heated at 100˚C till the generation of yellowish smoke ends. After that 50 ml distilled water is added and when it starts to boil, it is removed from the hot plate for filtration.

5. Filtrate is then analyzed at AAS.

Table A.4 Effect of collector type on Pb grade and recovery in galena concentrate

Collectors	Pb Grade (%)	Pb Recovery (%)
KAX	75.81	7.23
KEX	57.43	3.84
SIPX	71.45	6.01
Aerophine 3418A	53.27	4.53
Aerophine 3418A+KAX	71.39	7.04

Table A.5 Effect of collector dosage on Pb grade and recovery in galena concentrate

Collector Dosage (g/t)	Pb Grade (%)	Pb Recovery (%)
100	70.50	5.40
200	75.81	7.23

Table A.6 Effect of dosage and conditioning time of Na_2S on Pb grade and recovery in cerussite concentrate

Dosage of Na_2S (g/t)	Cond. Time (min.)	Pb Grade (%)	Pb Recovery (%)
1000	10	62.76	44.23
1000	15	60.69	74.90
1000	20	75.52	28.32
1500	10	60.72	47.86
1500	15	74.24	47.77
1500	20	73.62	35.68
2000	10	63.25	75.53
2000	15	65.13	65.41
2000	20	64.44	55.43

Table A.7 Effect of collector type on Pb grade and recovery in cerussite concentrate

Collectors	Pb Grade (%)	Pb Recovery (%)
KAX	63.25	75.53
KEX	67.98	17.80
SIPX	67.93	26.14
Aerophine 3418A	55.35	71.11
Aero 404+KAX	51.99	55.86
Aero 407+KAX	70.00	55.70

Table A.8 Effect of collector dosage on Pb grade and recovery in cerussite concentrate

Collector Dosage (g/t)	Pb Grade (%)	Pb Recovery (%)
300	60.86	44.27
400	63.25	75.53

Table A.9 The overall test results conducted to investigate the effect of collector on flotation of galena and cerussite

Collectors for Galena	Collectors for Cerussite	Galena Concentrate		Cerussite Concentrate		Middling		Tailing		Total Pb Recovery (%)
		Pb (%)	Zn (%)	Pb (%)	Zn (%)	Pb (%)	Zn (%)	Pb (%)	Zn (%)	
KAX	KAX	75.81	3.67	63.25	6.76	5.21	29.63	2.33	32.63	82.76
KEX	KEX	57.43	3.96	67.98	2.92	15.34	26.09	11.12	30.62	21.64
SIPX	SIPX	71.45	3.03	67.93	3.27	12.41	27.48	10.20	32.27	32.15
Aerophine 3418A	Aerophine 3418A	53.27	2.61	55.35	7.16	6.16	27.43	3.50	35.67	75.64
Aerophine 3418A+KAX	Aero 404+KAX	71.39	4.91	51.99	6.67	13.88	25.81	3.83	34.22	62.90
KAX	Aero 407+KAX	77.51	3.06	70.00	4.51	13.79	29.53	4.55	35.25	62.93

Table A.10 The overall test results conducted to investigate the effect of dosage and conditioning time of Na_2S on flotation of cerussite

Dosage of Na_2S (g/t)	Cond. Time (min.)	Cerussite Concentrate		Middling		Tailing		Total Pb Recovery (%)
		Pb (%)	Zn (%)	Pb (%)	Zn (%)	Pb (%)	Zn (%)	
1000	10	62.76	4.21	11.81	25.37	5.25	35.33	52.37
1000	15	60.69	5.97	6.75	27.08	1.96	35.26	82.53
1000	20	75.52	3.79	21.72	22.17	6.42	31.49	36.71
1500	10	60.72	3.12	19.24	22.81	3.43	35.48	56.86
1500	15	74.24	3.12	18.94	25.05	5.05	34.75	55.63
1500	20	73.62	3.88	14.43	24.26	7.22	33.00	43.75
2000	10	63.25	6.76	5.21	29.63	2.33	32.63	82.76
2000	15	65.13	4.40	6.96	27.93	3.72	36.58	72.35
2000	20	64.44	4.05	12.63	27.00	3.48	35.29	63.26

Table A.11 Effect of ZnSO$_4$ addition on Zn grade

	Zn (%) in Galena Conc.	Zn (%) in Cerussite Conc.	Zn (%) in Middling	Zn (%) in Tailing
Without ZnSO$_4$	3.67	6.76	29.63	32.63
With ZnSO$_4$	3.11	6.26	30.89	33.18

Table A.12 The result of pH adjustment prior to cerussite flotation

	Cerussite Concentrate		Middling		Tailing		Total Pb Recovery (%)
	Pb (%)	Zn (%)	Pb (%)	Zn (%)	Pb (%)	Zn (%)	
Without pH adjustment	63.25	6.76	5.21	29.63	2.33	32.63	82.76
pH 9.5	64.82	6.89	6.23	30.85	3.55	35.26	76.34