

RECOVERY OF ZINC AND LEAD FROM ÇİNKUR LEACH RESIDUES BY
USING HYDROMETALLURGICAL TECHNIQUES

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**RECOVERY OF ZINC AND LEAD FROM ÇINKUR LEACH RESIDUES BY
USING HYDROMETALLURGICAL TECHNIQUES**

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ABSTRACT

RECOVERY OF ZINC AND LEAD FROM ÇİNKUR LEACH RESIDUES BY USING HYDROMETALLURGICAL TECHNIQUES

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In this thesis, it was aimed to select and propose a feasible method, or series of methods, for the recovery of zinc (Zn) and lead (Pb) that are present in disposed ÇİNKUR leach residues having 12.43 % Zn, 15.51 % Pb and 6.27 % Fe. Initially, physical, chemical and mineralogical characterizations of the leach residues were done. Results of these analyses showed that lead was present as lead sulfate (PbSO_4), and zinc was present as zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), zinc ferrite (ZnFe_2O_4) and zinc silicate ($2\text{ZnO} \cdot \text{SiO}_2$) in the leach residues. Initially, water leaching experiments were carried out to determine water soluble amount of blended leach residue, and the maximum zinc recovery was obtained as 18 %. After these trials, sulphuric acid and brine leaching were used to recover zinc and lead, respectively. Firstly, due to the insufficient recovery in water leaching trials acid leaching experiments were done for zinc recovery and the parameters studied were acid concentration, reaction duration, leaching temperature and solid-liquid ratio (pulp density). About 72 % Zn was recovered after hot acid leaching by using 150 g/l H_2SO_4 at 95 °C in 2 hours with a pulp density of 200 g/l.

For lead recovery brine leaching experiments were done with the secondary leach residue obtained after H_2SO_4 leaching. In brine leaching experiments, NaCl concentration, pulp density (solid/liquid ratio), reaction duration and leaching temperature were chosen as variables. Effect of HCl addition was also investigated. In brine leaching while lead recoveries up to 98 % could be attained at a low pulp density in laboratory scale, the maximum recovery obtained was 84.9 % at a high pulp density (200 g/l) with 300 g/l NaCl concentration in 10 minutes at 95 °C.

Keywords: Leaching, leaching residue, leach recovery, lead, zinc

ÖZ

ÇİNKUR LİÇ ARTIKLARINDAN ÇİNKO VE KURŞUNUN HİDROMETALURJİK YÖNTEMLERLE KAZANILMASI

Rüşen, Aydın

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Bu tezde, Çinkur atık sahasında bulunan ve içerisinde % 12.43 Zn, % 15.51 Pb ve % 6.27 Fe ihtiva eden Çinkur liç artığından çinko ve kurşunun geri kazanılması için uygulanabilir bir proses geliştirilmesi amaçlanmıştır. Öncelikle artığın fiziksel kimyasal ve mineralojik incelemesi yapılmıştır ve bunun sonucunda artık içerisindeki kurşunun kurşun sülfat ($PbSO_4$) ve çinkonun çinko sülfat heptahidrat ($ZnSO_4 \cdot 7H_2O$), çinko ferrit ($ZnFe_2O_4$) ve çinko silikat ($2ZnO \cdot SiO_2$) hallerinde bulunduğu tesbit edilmiştir. Artığın karakterizasyonu belirlendikten sonra sudaki çözünürlüğünü belirlemek için deneyler yapılmıştır. Sonrasında ise artık içindeki çinko ve kurşunu kazanmak için sırasıyla sülfürik asit ve sodyum klorür liç deneyleri yapılmıştır. İlk olarak atık içindeki çinkoyu geri kazanmak için asit konsantrasyonu, reaksiyon süresi, liç sıcaklığı ve katı-sıvı oranı (pülp yoğunluğu) değişkenleri kullanılmış ve 150 g/l asit konsantrasyonu, 95 °C liç sıcaklığı, 2 saat reaksiyon süresi ve 200g/l pülp yoğunluğu şartları altında %72 verim ile çinko kazanılmıştır.

Asit liç sonrasında içerdiği çinkonun büyük bir kısmı alınan ve böylece içerdiği kurşun oranı yükselen ikincil artık sodyum klorürle liç edilerek kurşun geri kazanımı

sađlanmaya alıřılmıřtır. Yapılan deneylerde alıřılan parametreler NaCl konsantrasyonu, katı-sıvı oranı, reaksiyon süresi ve li sıcaklıđıdır. Ayrıca, hidroklorik asit (HCl) ilavesinin sistem üzerindeki etkisi de incelenmiřtir. Sonuçta düşük pülp yoğunluklarında % 98 gibi yüksek kurřun geri kazanımı sađlanmasına rađmen yüksek pülp yoğunluklarında (200g/l) 300 g/l NaCl konsantrasyonu, 95 °C li sıcaklıđı ve 10 dakika li süresi için en yüksek kurřun li verimi % 84,9 olarak elde edilebilmiřtir.

Anahtar Kelimeler: Li, li artıđı, li verimi, kurřun, inko

**To My Wife,
and My Parents**

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CHAPTER I

INTRODUCTION

Zinc and lead have been known and used by humans since ancient era [1]. Today, they are the most important nonferrous metals after copper and aluminum [2]. Zinc and lead have different properties thus they are used in various application areas from automobiles to construction, batteries to textile and so on [3, 4].

Zinc and lead deposits are widely distributed in the Earth's crust. Zinc sulfide namely Sphalerite (ZnS), is the principal ore mineral for zinc and lead sulphide known as Galena (PbS), is the main source of lead in the world [5].

Although zinc is generally produced from sulphidic ores (ZnS) or concentrates by Roast –Leach – Electrowinning (RLE) [6] in the world, in Turkey, zinc production is based on zinc carbonate ores ($ZnCO_3$), at Çinkur plant from establishment to 1997 due to high reserves of zinc carbonate. Çinkur is the only plant in Turkey that produces Zn from primary ore containing $ZnCO_3$ by Waelz – Leach - Electrowinning route [7]. However, due to depletion of local high grade ores, oxidized ore concentrates were imported from Iran after 1997 until this plant was shut down. Therefore, there are two different leach residues (LR) which are Turkish LR (TLR) and Iranian LR (ILR) in Çinkur stockpiles. It has been estimated that the total amount of leach residue is more than one million tons of which the major part is Turkish leach residue (TLR).

Considering more than one million tons leach residue rich in Zn (11-13%) and Pb (15-17%) in the stockyard it is essentially necessary to process Çinkur LR. In addition, a previous study [8] on heavy metal pollution potential of discarded leach residues in Çinkur Plant showed that the leach residues are hazardous wastes for the environment.

Mainly, pyrometallurgical and hydrometallurgical methods or their combination can be used for treating secondary materials or residues [9]. The hydrometallurgical processes are regarded as more eco-friendly to treat such materials having low zinc content. Hydrometallurgical method is more suitable to process such a residue because all pyrometallurgical operations have high thermal requirements, elaborate dust collecting systems and require additional processing to separate the lead and zinc as products [10]. In addition, hydrometallurgical processes can much easily be adapted to the present plant.

In this study, zinc and lead recovery from zinc plant leach residue obtained from Çinkur using hydrometallurgical methods have been investigated by laboratory scale experiments. Zinc and lead have been recovered in two main stages. As a first step, Çinkur leach residue was re-leached by using hot sulphuric acid for zinc recovery. Secondly, for lead recovery brine (sodium chloride) leaching tests were performed on the secondary Çinkur leach residue obtained after acid leaching process. As a result, the possible process parameters for zinc and lead recovery were determined.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1. Introduction

In this chapter, the basic information of zinc and lead is given starting from their histories to properties and their sources. Production methods of lead and zinc are presented in detail. In addition, some of the application areas of lead and zinc are given. Lastly, the previous studies about leach residues in Turkey and in the world are summarized.

2.2. Zinc

2.2.1. History

History of zinc starts from 5000 years ago and goes to nowadays. In early times zinc was known as the alloy of brass, combination of copper and zinc. After centuries zinc was discovered by metallurgists of India in metallic form and then the production of zinc metal was very common in the ancient India. At the end of the thirteenth century, zinc manufacture moved from India to China. Following centuries Chinese miners learned and developed production of zinc. On the other hand, European scientists were aware of the existence of this new metal which had different properties from other known metals and Paracelsus was credited with the name “zinc” at 16th century.

During middle of the eighteenth century, zinc technology was transferred from China to Britain where patenting a process to extract zinc from calamine (mineral source of zinc metal) in a smelter. After a few years, the production of zinc was started from sulphide ores. At 1798, wastes obtained from various sources that included zinc were processed to produce zinc.

The first commercial electrolysis process was introduced in U.S.A. in 1916. After a few years, an important development was made in the zinc industry. This was ZnO production by using the Waelz process which produced ZnO from low grade carbonate ores and other oxide or oxidized sources.

Nowadays, the use of pyrometallurgical route in zinc production lost its importance with the development of Roast-Leach-Electrowinning and Pressure Leaching processes [11-15].

2.2.2. Properties

The chemical symbol for zinc is Zn, its atomic number is 30 and its atomic mass is 65.39. Naturally, five stable isotopes of zinc are known. Zinc is a transition metal with bluish pale gray color. It shows very good thermal and electrical conductivity. In addition, it is extremely brittle at ordinary temperatures but becomes malleable between 120 and 150°C. Due to this feature, it could be rolled into sheets between these temperatures [1, 11, 14]. Other physical, atomic and miscellaneous properties of zinc are given in Table 2.1.

2.2.3. Sources of Zinc

Zinc is widely dispersed in the earth's crust in different forms. The most important ore minerals are sulphide type (ZnS), zinc blend or sphalerite; carbonate type (ZnCO₃), zinc spar or smithsonite; and silicate type (Zn₂SiO₄), willemite. Other zinc minerals such as calamine, franklinite, etc. are less important. Zinc minerals listed in Table 2.2 mostly exist with lead and other valuable metals (silver or gold) [11].

Table 2.1: Properties of Zinc [11, 15]

| | | | |
|-------------------------|------------------------|--|----------------|
| Solid Density (at RT) | 7.14 g/cm ³ | Ionization energies (1 st) | 1733.3 kJ/mole |
| Liquid Density (at MP) | 6.57 g/cm ³ | Ionization energies (2 nd) | 1733.3 kJ/mole |
| Melting Point | 419.5°C | Atomic radius | 135 picometer |
| Boiling Point | 907°C | Magnetic ordering | Diamagnetic |
| Heat of fusion | 7.32 kJ/mol | Electrical resistivity (20°C) | 59 n.Ω.m |
| Heat of vaporization | 123.6 kJ/mol | Thermal conductivity (20°C) | 116 W/m.°K |
| Heat capacity (at 25°C) | 25.390 J/mol °K | Thermal expansion (25°C) | 30.2 μm/ m.°K |
| Crystal structure | Hexagonal | Young's modulus | 108 GPa |
| Oxidation States | 2 | Shear modulus | 43 GPa |
| Electronegativity | 1.65 (Pauling S.) | Mohs hardness | 2.5 |

Table 2.2: Zinc Mineral Types [11]

| Mineral | Chemical Formula | Zinc content, % |
|-------------------------|--|------------------------|
| Sphalerite | ZnS | 67.0 |
| Marmatite | (Zn,Fe)S | 45.0 |
| Smithsonite | ZnCO ₃ | 52.0 |
| Calamine (Hemimorphite) | Zn ₄ Si ₂ O ₇ (OH) ₂ .H ₂ O | 54.2 |
| Hydrozincite | Zn ₅ (OH) ₆ (CO ₃) ₂ | 56.0 |
| Zincite | ZnO | 80.3 |
| Willemite | Zn ₂ SiO ₄ | 58.5 |
| Franklinite | (FeZnMn)(FeMn) ₂ O ₄ | 15-20 |

The average level of zinc in the earth's crust is 83 g/t [11]. In some areas, zinc level reaches up to 300 g/t [5]. Although zinc ores are found in more than 50 countries, the major parts of zinc deposits are present in China, Canada, Australia, Peru and USA [16]. Amount of zinc reserves in thousand tons and zinc mine production in metric tons of zinc content terms for leading countries in the world are given in Table 2.3.

There are approximately 2,400,000 tons of zinc mine reserve and reserve base in different regions of Turkey [17]. Apart from sulphidic ores, the reserves contain zinc carbonate ($ZnCO_3$) mineral. Zinc reserves of Turkey is 1.28% that of in the world. Map of zinc and lead areas is given in Figure 2.1. Lead-zinc deposits in Turkey can be divided into three main groups based on chemical content. These are Pb-Zn, Pb-Zn-Cu and Cu-Pb-Zn-Ag [18]. In the eastern Black Sea, around of Çayeli-Madenköy, sulphidic zinc deposits are found together with copper and lead. On the other hand, Zamantı and Bolkarlar Regions in the Central Anatolia are very rich in smithsonite (zinc carbonate) with lead carbonate and small amount of cadmium. [17].

Table 2.3: Zinc Mine Reserves and Zinc Mine Production in the World [16]

| COUNTRY | 2003 (tons) | 2004 (tons) | 2005 (tons) | 2006^e (tons) | Reserves (1000 tons) | Reserve Base (1000 tons) |
|-----------------|-----------------------|-----------------------|-----------------------|-----------------------------------|--------------------------------|------------------------------------|
| China | 2,030,000 | 2,390,000 | 2,450,000 | 2,500,000 | 33,000 | 92,000 |
| Australia | 1,447,000 | 1,298,000 | 1,329,000 | 1,400,000 | 33,000 | 80,000 |
| Peru | 1,372,790 | 1,209,006 | 1,201,671 | 1,210,000 | 16,000 | 20,000 |
| Canada | 757,307 | 735,698 | 755,000 | 725,000 | 11,000 | 31,000 |
| United States | 767,597 | 738,876 | 748,000 | 725,000 | 30,000 | 90,000 |
| Mexico | 413,991 | 426,330 | 470,000 | 450,000 | 8,000 | 25,000 |
| Kazakhstan | 395,000 | 360,000 | 400,000 | 450,000 | 30,000 | 35,000 |
| Other countries | 1,825,641 | 1,795,630 | 1,964,477 | 2,350,000 | 59,000 | 87,000 |
| World total | 9,468,326 | 9,459,196 | 9,795,148 | 9,860,000 | 220,000 | 460,000 |

e: Estimated

Another important point is the formation of SO_2 in pyrometallurgical ones. If SO_2 is not enough to make H_2SO_4 , then its disposal is a very big problem. Although extra energy is required to treat low grade ores due to presence of high amount of gangue minerals in the pyrometallurgical method, this problem could be eliminated by using a selective leachant in the hydrometallurgical ones. Lastly, hydrometallurgical operations are performed in small scale and need lower capital investment than those of pyrometallurgical.

2.2.4.1. Pyrometallurgical Methods

Due to the advantages of hydrometallurgical method, only a small part of zinc production is continued by pyrometallurgical route. Figure 2.2 shows use of zinc production methods. There are two main pyrometallurgical processes, Imperial Smelting Process (ISP) [21] and Retort Process (RP) [22] to extract zinc from ore.

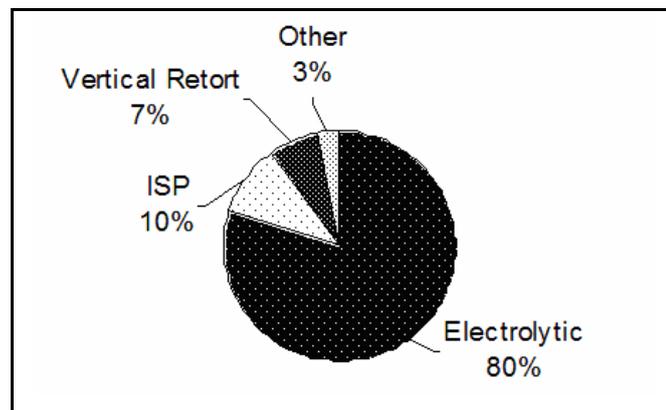


Figure 2.2: Use of Zinc Production Methods [16]

2.2.4.1.1. Imperial Smelting Process

ISP is a more common pyrometallurgical method in extraction of zinc because of simultaneous production of lead and zinc. In retort process, however, only one metal is extracted i.e., only zinc. Moreover, in ISP method, a mixture including

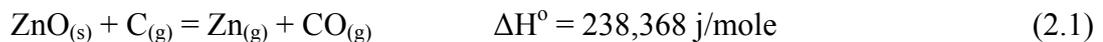
Zn-Pb sinter is charged to furnace and lead is tapped conventionally from the bottom, on the other hand, vapor zinc is condensed in metallic form.

Zinc and lead metal are produced by reducing their oxides with carbon or carbonaceous materials in imperial smelting furnace which is like an iron blast furnace. Preheated charge materials are added to the furnace from the top. The charge to the blast furnace is lump sinter and coke, the coke burning in the lower part of the shaft and the heat from this and the carbon monoxide gas produced providing the means to reduce the zinc and lead oxides to metallic zinc and lead. While zinc evaporates due to its lower boiling point, lead goes to the bottom of the furnace together with copper, silver and other metals. Zinc fume should be condensed as soon as possible. Otherwise, it will be converted to zinc oxide.

Due to the special relationship between lead and zinc, by cooling the lead, crude zinc is released and is separated, and the lead returns to the “condensing” process for another cycle of dissolving and then releasing more zinc.

2.2.4.1.2. Retort Process

Although there are two types of zinc retort as vertical and horizontal, today; mainly vertical retort is used to extract zinc. This is because of the fact that vertical retort enables continuous operation and has larger production capacity. Main step in vertical retort is to reduce ZnO by coke and to obtain Zn fume according to reaction (2.1).



Since this reaction is endothermic, heat must be supplied up to required temperature, 1300°C. As the reaction proceeds, zinc metal evaporates and zinc fumes start to form as a reaction product. At the end of this process, condensed zinc is obtained and casted as ingots with high recovery.

2.2.4.2. Hydrometallurgical Methods

In the world, over 90% of zinc production is from the primary sulphide ores processed by Roast – Leach – Electrowinning route, but in Turkey, zinc ores are treated in Waelz – Leach – Electrowinning sequence at Çinkur due to the fact that reserves contain zinc carbonate ($ZnCO_3$). As a result, hydrometallurgical extraction of zinc can be summarized in two subsections for sulphidic ores and carbonated ores.

2.2.4.2.1. Production of Zinc from Sulphidic Ores

Zinc is generally produced from primary sulphide ores. Hydrometallurgical zinc extraction for sulphidic ores is operated by either conventional [21] or pressure leaching [9] methods.

i) *Conventional Leaching*

Zinc concentrate obtained after flotation can be treated by leaching in batch or continuous processes. Figure 2.3 shows the flowsheet for a simple electrolytic zinc process called as “single leaching”. For sulphide type zinc concentrate, roasting is the first step in this process. In roasting, ZnS reacts with oxygen according to reaction (2.2). At the end of reaction zinc calcine (ZnO) is obtained and released SO_2 is sent to acid plant to produce sulphuric acid.



During leaching, calcine is added to the spent electrolyte up to achieving the minimum acid concentration to be able to dissolve zinc. In order to remove iron and other impurities, pulp is neutralized with lime. In acid leaching, ZnO is converted to the water soluble $ZnSO_4$ according to reaction (2.3). After filtration pregnant solution is obtained. This impure solution is then purified by adding scrap or zinc dust, which precipitates the dissolve impurity metals by cementation. When the solution leaves the purification section, it passes to the electrolytic tank house to obtain high purity metallic zinc. In this step, reaction (2.4) given below takes place.

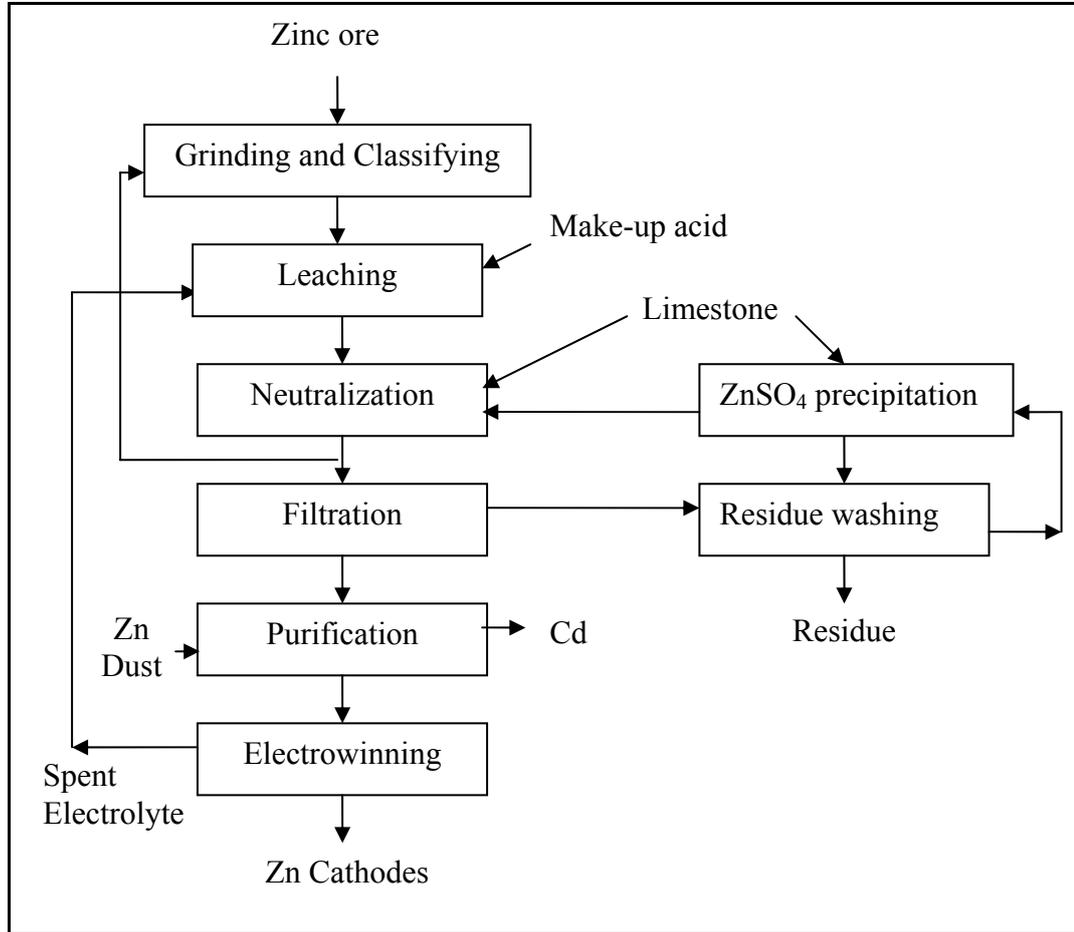


Figure 2.3: The Basic Flowsheet of Electrolytic Zinc Process [21]

Depending on technological improvements, “double leaching” process, shown in Figure 2.4, is developed. Mainly, this process resembles to single leaching, but it has two leaching steps. In first stage, excess calcine is added until all the acid in the electrolyte is consumed, in the meantime iron and other impurities are precipitated. Second leaching stage is done by low acid solution. After that solution comes back to first leach step and leach residue is discarded. Most of the electrolytic zinc plants operate by using this process.

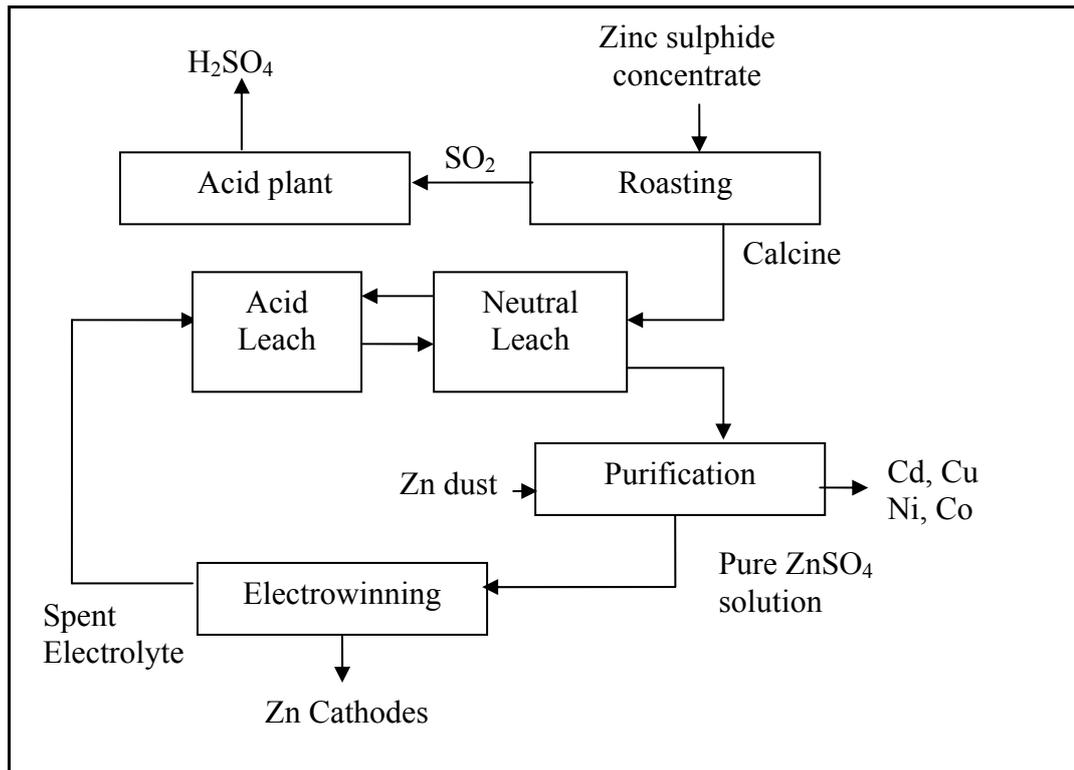


Figure 2.4: Double Leaching Zinc Processes [21]

ii) *Pressure Leaching*

Since sphalerite is directly leached with sulphuric acid in this process, it is called as “direct leaching of zinc concentrate” or as Sherritt-Gordon zinc acid pressure leach process. As compared to conventional process, direct leaching process has some advantages. First of all, the roasting stage is discarded which prevents the formation of complex zinc ferrite. In addition, low grade ores can be evaluated by direct leaching even in the presence of high iron in ore. Other positive aspect is low capital cost of this process. Related flowsheet with the direct leaching is given in Figure 2.5.

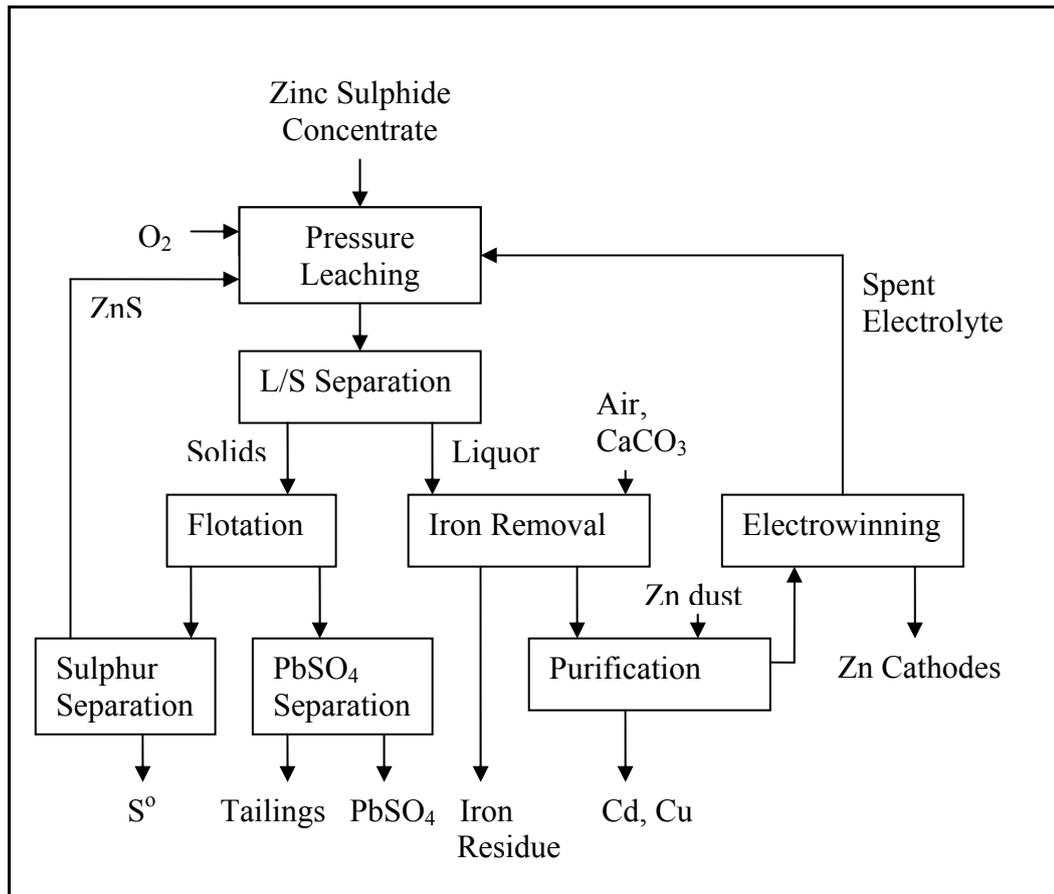


Figure 2.5: Zinc Acid Pressure Leach Process [9]

By using this process, any valuable metal can be obtained with various leachants. In Figure 2.5, the required procedure is given for the recovery of zinc from concentrate by using sulphuric acid as leachant. Concentrate should be finely ground to - 44 microns so that all particles react with sulphuric acid. Overall reaction (2.5) that occurs in autoclaves is as follows:



After leaching, leach liquor is sent to iron removal process and then purification stage. Finally, zinc metal is obtained via electrowinning and spent electrolyte returns to first stage. For typical pressure leaching maximum temperature should be lower than 150°C and minimum oxygen partial pressure should be higher than 2 bar. By the use of these conditions, over 97% zinc extraction can be obtained.

2.2.4.2.2. Production of Zinc from Carbonated Ores

As mentioned before, in Turkey zinc reserves contain high amounts of smithsonite (ZnCO_3). Carbonate ores are very difficult to concentrate by flotation or other mineral processing techniques. Therefore, these ores need a pyrometallurgical pretreatment to be able to convert ZnCO_3 to ZnO . Waelz kiln technology [23] has been used for this pretreatment. Actually, Waelz process is designed for the treatment of low grade and complex ores and it is applicable to all ores containing zinc, lead, cadmium, etc.

Average length of Waelz furnace and interior diameter is 70 m and 4.3 m, respectively. Waelz furnace feeds crushed ore and calculated amount of suitable reducing agent, coke or coal. In the kiln, a long period reaction occurs between the charge and reducing agents. Moreover, this enables complete decomposition of all zinc compounds. In such a strong reducing atmosphere, together with the effect of heating, metals in the charge are volatilized, and then these metallic vapors are oxidized in kiln. Reduction of zinc oxide consumes much heat which is supplied by oxidation of zinc vapor. All these events occur between 900 and 1300°C. At the end of Waelz process, oxidized metals (ZnO , PbO , CdO) called as waelz oxide are obtained. After densifying stage which requires removing volatile elements like Cl and F, the production line resembles to other leaching processes explained above as shown in Figure 2.6.

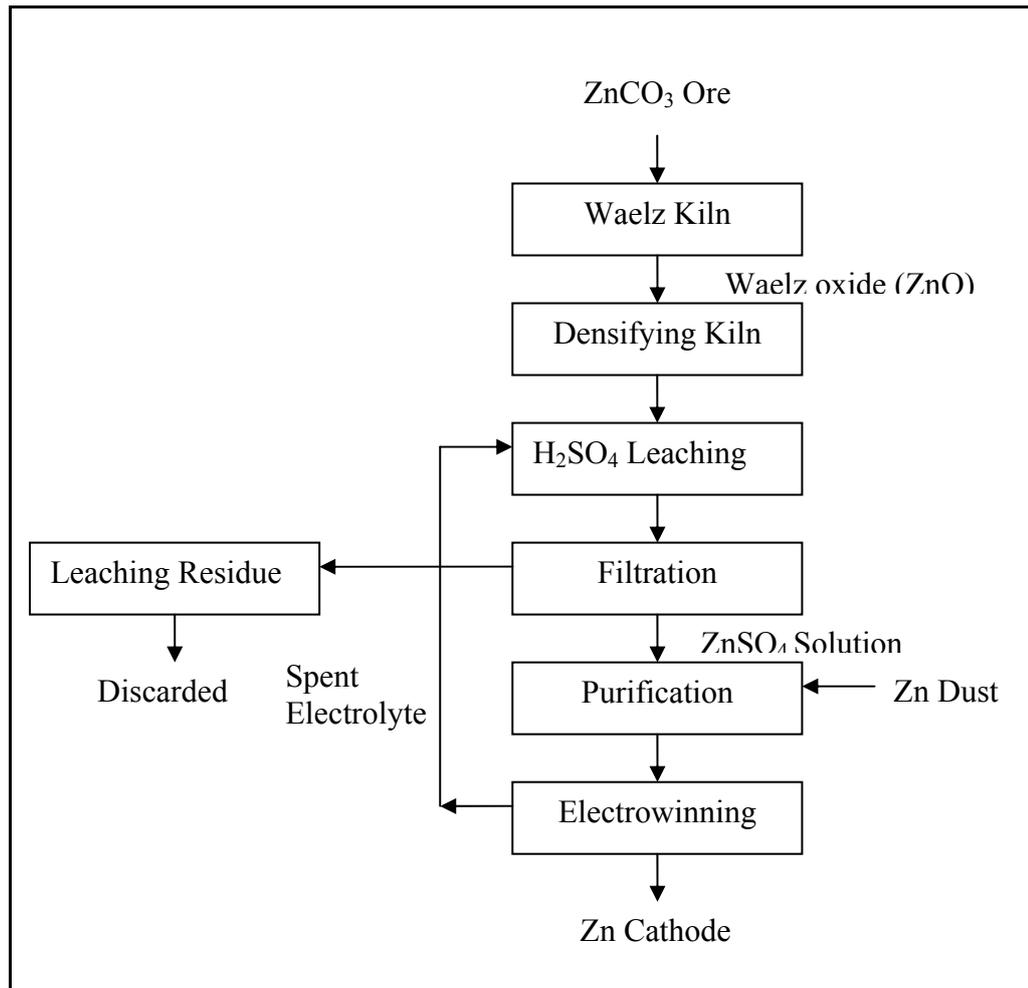


Figure 2.6: Electrolytic Zinc Production from Smithsonite Ore [3]

2.2.5. Applications of Zinc

Zinc is an important base metal required for various applications in metallurgical, chemical and textile industries. As shown in Figure 2.7, the main application for zinc is galvanizing which accounts for about 49% of worldwide zinc use. In order to protect steel against corrosion, the most effective and economical way is zinc coating, called galvanizing. Compared to the other materials, galvanized steel has lots of advantages such as corrosion resistance, high strength, light weight and low cost. Due to all of these properties galvanized steel is used in various applications from automobiles to commercial and industrial constructions.

In addition, zinc alloys are the other application areas. Zinc casting alloys are used in mechanical parts due to their special high hardness, self lubricating properties, and dimensional stability and so on. Since zinc has excellent thermal and electrical conductivity, casting alloys also can be used for electrical components and heating equipments. ZAMAK and ZA alloys are the basic zinc casting alloys. ZAMAK includes about 4% Al, which gives good strength and excellent die castability. Therefore, most of the zinc die castings are produced with ZAMAK alloys.

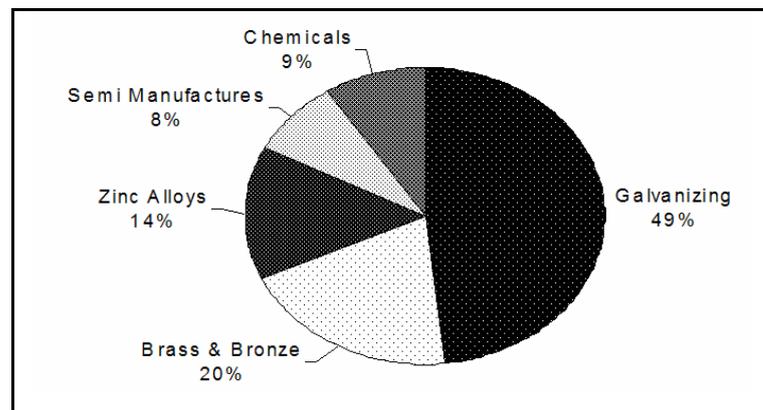


Figure 2.7: End Uses of Zinc [7]

Brass is another material in the field of zinc applications. It includes copper and zinc ranging from %10 to %50 Zn. Zinc as brass is mainly used in decorative objects, door handles and interior design materials.

Zinc compounds have several applications in various industries. For example they are used in alkaline batteries and dry batteries as well as in purification stage as cement agent. Main zinc compound is zinc oxide used in the manufacture of paints, pharmaceuticals, soap, textiles, electrical equipment and many other application products.

In the 20th Century, except for mentioned above, zinc plays very important role in many of the major inventions from transistors to lasers, satellites to circuit boards,

photocopiers to fuel cells, and zinc is really among the most versatile and essential materials known to mankind [1-5, 15, 16].

2.3. Lead

2.3.1. History

Lead is a well-known metal and has been used by mankind for thousands of years due to its easy extraction and smelting properties. The oldest lead piece is in the British Museum and dates from 3800 B.C. Metallic lead is known to be produced by the Chinese about 3000 B.C. Lead was used for plumbing by the Romans and used for lining of tea chest by the Chinese. It was also utilized by Egyptians in glazing pottery. Most of the oldest applications are still in use. Lead's symbol Pb comes from its Latin meaning "plumbum" which means soft metal.

In the early 1700s, the lead foundries developed in Great-Britain, and after a short time first lead production started in the U.S.A. In the 1860s, new developments of the lead technology greatly lowered production costs and increased productivity within the lead industry [1, 5, 12, 23, 24].

2.3.2. Properties

Lead, represented by Pb, has atomic number of 82 and its color is bluish-white. Natural lead has four stable isotopes. Pure lead has low mechanical strength. It is also extremely soft and malleable. In addition, lead is a dense and ductile metal. Atomic weight of lead is 207.2. It shows high resistance to corrosion but poor electrical conductivity. Since lead is a heavy metal, it is hazardous for human health and environment. The main properties of lead are summarized in Table 2.4 [1, 3, 24].

Table 2.4: Properties of Lead [3, 5, 24]

| | | | |
|-------------------------|-------------------------|--|----------------|
| Solid Density (at RT) | 11.34 g/cm ³ | Ionization energies (1 st) | 715.6 kJ/mole |
| Liquid Density (at MP) | 10.66 g/cm ³ | Ionization energies (2 nd) | 1450.5 kJ/mole |
| Melting Point | 327.5°C | Atomic radius | 180 picometer |
| Boiling Point | 1749°C | Magnetic ordering | Diamagnetic |
| Heat of fusion | 4.77 kJ/mol | Electrical resistivity (20°C) | 208 n.Ω.m |
| Heat of vaporization | 179.5 kJ/mol | Thermal conductivity (20°C) | 35.3 W/m.°K |
| Heat capacity (at 25°C) | 26.650 J/mol °K | Thermal expansion (25°C) | 28.9 μm/ m.°K |
| Crystal structure | Cubic Face Centered | Young's modulus | 16 Gpa |
| Oxidation States | 2, 4 | Shear modulus | 5.6 Gpa |
| Electronegativity | 2.33 (Pauling S.) | Mohs hardness | 1.5 |

2.3.3. Sources of Lead

Mainly, lead is found in the earth's crust as sulphide (PbS), also called galena. Other lead forms in the nature are sulphate (PbSO₄) and carbonate (PbCO₃). All of the lead minerals are given in Table 2.5 [22].

Table 2.5: Lead Mineral Types [21]

| Mineral | Chemical Formula | Lead content, % |
|----------------------|--|-----------------|
| Galena (lead glance) | PbS | 86.6 |
| Cerussite | PbCO ₃ | 77.5 |
| Anglesite | PbSO ₄ | 68.3 |
| Jamesonite | Pb ₂ Sb ₂ S ₅ | 50.8 |
| Pyromorphite | Pb ₅ Cl(PO ₄) ₃ | 76.4 |
| Vanadinite | (PbCl)Pb ₄ (VO ₄) ₃ | Variable |
| Desclozite | 4(PbZn)O.V ₂ O ₅ .H ₂ O | Variable |

Galena including only a few grams silver per ton ore is widely dispersed in the world [23]. The main sources are the U.S.A., China, Australia, Spain, Mexico, and Germany. Depending on data given in ILZSG (International Lead and Zinc Study Group), January 2007 [5] Asia is the leading world lead producer and consumer. Lead production and reserves values in the world according to leading countries are given Table 2.6.

Table 2.6: Zinc Mine Reserves and Zinc Mine Production in the World [16]

| COUNTRY | 2003 (tons) | 2004 (tons) | 2005 (tons) | 2006^e (tons) | Reserves (1000 tons) | Reserve Base (1000 tons) |
|-----------------|-----------------------|-----------------------|-----------------------|-----------------------------------|--------------------------------|------------------------------------|
| China | 995,000 | 998,000 | 1,000,000 | 1,050,000 | 11,000 | 36,000 |
| Australia | 690,000 | 678,000 | 776,000 | 780,000 | 15,000 | 28,000 |
| United States | 448,600 | 430,000 | 426,500 | 426,000 | 8,100 | 20,000 |
| Peru | 307,700 | 306,200 | 319,300 | 320,000 | 3,500 | 4,000 |
| Mexico | 139,500 | 118,500 | 130,000 | 140,000 | 1,500 | 2,000 |
| Canada | 93,000 | 71,000 | 72,500 | 79,000 | 2,000 | 9,000 |
| Other countries | 466,200 | 508,300 | 546,200 | 565,000 | 26,000 | 41,000 |
| World total | 3,140,000 | 3,110,000 | 3,270,000 | 3,360,000 | 67,000 | 140,000 |

e: Estimated

Usually, lead ores contain 1-10% lead; however, the treatment of ore having lower than 3% lead may not be economical. In order to increase lead content, ores should be crushed and concentrated generally by flotation. At the end of these treatments concentrate can contain up to 70% lead [22].

As mentioned in zinc sources part, in Turkey lead is generally associated with zinc deposits. The clearest evidence for this situation is Figure 2.1. In Turkey, the amount of lead ore reserve is estimated to be about 1,800,000 tons which corresponds to 1.33% of the world reserve [18].

2.3.4. Extraction of Lead

2.3.4.1. Pyrometallurgical Lead Extraction

Lead production mostly depends on lead sulfide, galena, and through pyrometallurgical reduction-extraction routes. Pyrometallurgical lead extraction method can be divided into two sub-sections; Conventional [23] and Direct Smelting Process [25]. Use of Lead Production Methods in the world is shown in Figure 2.8. Today, it is seen that most of the lead is produced by conventional blast furnace method.

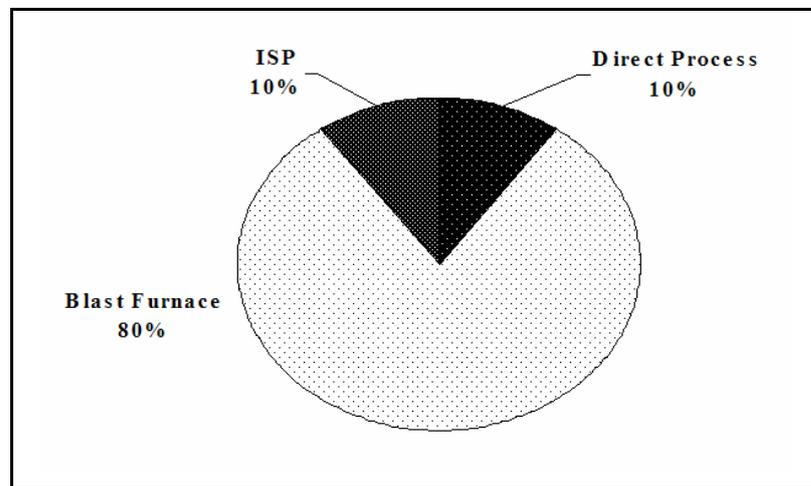


Figure 2.8: Use of Lead Production Methods [3]

2.3.4.1.1. Conventional Smelting Process

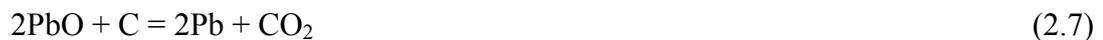
In this method, pyrometallurgical extraction of lead from ore or concentrate is carried out by reduction smelting in either a lead blast furnace or more complex ISP. If reserve includes both zinc and lead minerals, ISP can be used for simultaneous production of lead and zinc. In conventional smelting process, first step is roasting which enables to transform lead sulphide to the oxide form. In order to achieve this purpose a Dwight Lloyd Sintering Machine is used. This machine

supplies feed suitable for the blast furnace. Feed includes lead sulphide concentrate, returned sintering fines and limestone flux.

Lead blast furnace requires high amount of heat in order to reduce lead oxide. Most of the required heat is supplied by the combustion of carbon. After combustion of carbon, carbon monoxide is formed. Beginning at a temperature of about 400°C, the CO produced lower down in the furnace reduces the lead oxide according to reaction (2.6) thus liberated lead trickles down over the particles of undecomposed ore, absorbing precious metals as well as a part of arsenic, copper and antimony.



At about 600-700°C, iron oxide in the charge is reduced by CO and this iron decomposes lead sulphide and oxide. Lead is also formed by direct reduction of carbon and by the reactions between lead sulphide and oxide as seen in reactions (2.7-2.9)



Finally, metal and slag is completely liquid at temperatures higher than 1000°C, and lead is tapped from the furnace.

2.3.4.1.2. Direct Smelting Processes

Due to environmental problems and inefficient energy usage of the conventional processes, researchers studied to develop more economical and less pollution processes for the production of lead. Some of them aimed at devising processes in which lead is converted directly from the sulphide to metal. Main advantage of these processes is that PbS transforms to PbO without initial step. Consequently, several direct smelting processes, Kivcet, QSL (Queneau-Schuhmann-Lurgi), Ausmelt and Outokumpu, have been developed.

i) *Kivcet*

Kivcet[®] method based on the Soviet technology is a direct smelting process. Since simultaneous production of zinc and lead is possible in this method, it is suitable for complex ores with high zinc contents. After grinding and drying, sulphide concentrate and flux are injected to furnace with technically pure oxygen. So, the roasting and smelting stages are carried out, simultaneously. Liquid metal and slag pass from the smelting shaft into electric furnace to reduce oxides to metal by the addition of coke. At last, metallic materials are tapped from the furnace. Zinc and lead can be recovered at about 85% and 99% efficiency, respectively.

Kivcet[®] method has some advantages;

- Handling of dried lead-bearing charge and hence the formation of dust is kept to a minimum,
- Having smaller process off-gas volumes due to using pure oxygen instead of air,
- SO₂ concentration is high to produce sulphuric acid [3].

ii) *QSL*[®]

QSL (Queneau – Schuhmann – Lurgi) process is a continuous process. In this process, sulphide concentrate, return flue dust and flux are continuously mixed with a little water and compacted into pellets which are dropped directly into the oxidation zone of the reactor. The pellets dissolve rapidly in the resulting molten bath and are partially oxidized lead to lead oxide by submerged injection of oxygen. Oxidation is autogenous at the operating temperature of 950 - 1000^oC and the evolution of lead fume is low. At the end of process metallic lead is tapped continuously with a little copper and silver. Slag containing lead oxide and other metal oxides is also continuously discharged in opposite direction of the matte. Lead content in the slag is about 2%.

QSL process has the same advantages with Kivcet, i.e., low off gas volume and high SO₂ concentration. There is one extra advantage; QSL process is very suitable

for the environment. Since all raw materials are handled in a moist state there is little opportunity for dust evolution [3, 25].

iii) *Ausmelt*[®]

The Ausmelt process originated in Australia is developed by using Sirosmelt[®] lance technology. The Isasmelt (Ausmelt) process for lead is a fully continuous two stage process which is based on gas injection into melts via a top entry submerged Sirosmelt lance. Submerged injection produces turbulent baths in which high intensity smelting or reduction reactions may occur. In the first stage of the process, lead concentrate is added directly to a molten slag bath and is oxidized by air injected down the lance. Simultaneously, the high lead slag from this furnace is continuously transferred down a launder to a second furnace and reduced with coal. The crude lead product and discard slag are tapped continuously from the reduction furnace through a single taphole and separated in a conventional forehearth. This process provides several advantages i.e. compact vessels, durable submerged lances, good hygiene, simple control and operation and so on. [3]

iv) *Outokumpu*[®]

This process was developed in Finland to treat copper concentrates and has become standard technology in that field. It is a flash or suspension smelting process that uses technical oxygen to burn sulphur and fuel. Drying, flash smelting, slag cleaning and gas handling are the main parts of this process. After mixing, lead concentrate and fluxes are dried and fed to flash smelting. In flash furnace concentrate is oxidized and then smelted directly into the lead bullion and slag. Quality of lead bullion depends on degree of oxidation. Process needs a small gas cleaning step owing to low gas volume and high concentration of SO₂ which is suitable for sulphuric acid manufacture [25].

2.3.4.2. Hydrometallurgical Lead Extraction

In order to benefit from advantages of hydrometallurgical method many researchers studied hydrometallurgical treatment of primary or secondary sources of

lead and a few processes have been developed. However, none of them is applicable and economic compared with pyrometallurgical processes. Several facts have contributed to limit its application. The most important fact is that pyrometallurgical processes are simpler and cheaper and also highly pure product can be produced by using this method. In addition, suitable reagent has not been found to dissolve directly sulphide ores. Therefore, hydrometallurgical lead extraction has not been practiced industrially on a large scale.

Nevertheless, direct leaching of lead sulphide was tested at pilot plant scale. Leaching of lead sulphide concentrates usually occurs in the presence of a concentrated solution of NaCl. A complex lead chloride (PbCl_4^{2-}) is formed according to reaction (2.10).



In order to separate the gangue minerals, hot filtration step is needed. After filtration, solution is cooled to crystallize pure PbCl_2 which is then separated and sent to fused salt electrolysis step to recover lead and chlorine [20].

Other possible processes required a pretreatment step. Converting sulphide ores to the sulphate by roasting process with sulphuric acid at low temperature (400-500°C), soluble compound (PbSO_4) can be obtained and dissolved by a saturated sodium chloride solution. At the end of this process, lead chloride (PbCl_2) produced is separated and electrolyzed in the fused state to obtain lead [21].

2.3.5. Applications of Lead

Lead is widely used in various industries both as the metal and as its chemical compounds such as lead chromate, lead molybdate, tetraethyl lead and tetra methylene lead (TEL and TML). As shown in Figure 2.9, major application of lead in the world is lead-acid battery used on a large scale in car batteries. Demand for lead increased with increasing production of vehicles and using of starting-lighting-ignition (SLI) lead acid storage batteries. Today, over 80% of the total lead consumption is spent in SLI type batteries which are used in industrial forklifts,

airport ground equipment, mining equipment, as well as stationary sources of power in uninterruptible power systems (UPS) for hospitals, computer and telecommunications networks.

For example, in the USA, 88% of the total lead consumption is spent by lead-acid storage batteries. Other uses are ammunition (3%), oxides in glass and ceramics (3%), casting metals (2%), and sheet lead (1%). The remainder was consumed in solders, bearing metals, brass and bronze bullets, covering for cable, and extruded products.

Another important application of lead is radiation shielding in high energy radiation fields. Due to its high density and high atomic number, lead is used in shielding applications. Moreover, lead in powder form is used as a material for protective clothing in plastic and rubber sheeting.

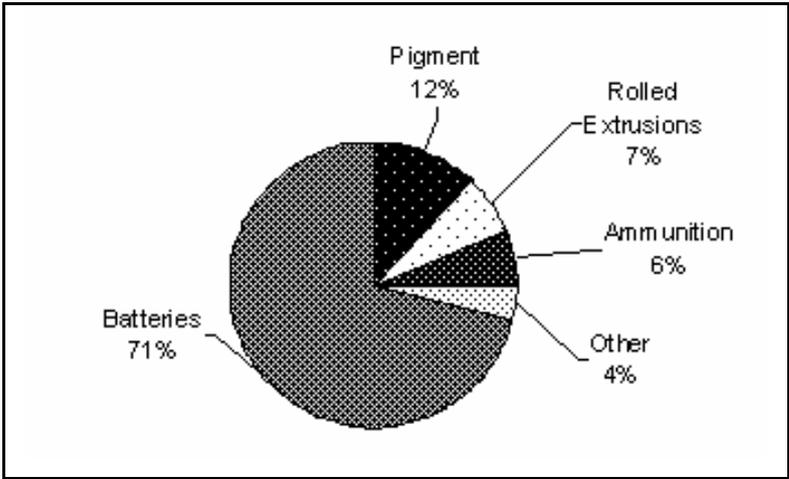


Figure 2.9: End Uses of Lead [7]

Since lead is a dense metal and has low cost compared to alternative products, it is used as projectiles (bullets) for firearms. In the past, lead was used as a pigment in paint industry. Afterwards, its usage was prohibited due to the hazards caused for the human health. However, some lead compounds, lead chromate (yellow), lead

molybdate (red) are still in use in road markings and plastics, respectively. In addition, lead as coloring element gives white and red color to ceramic glazes.

Other lead compounds are tetraethyl and tetra methylene lead (TEL and TML). These compounds are used in gasoline to increase octane rating and so provide the grade of gasoline required for the efficient operation. In order to extend the temperature range for rigid and plasticized PVC, tri or tetra basic lead sulphate is used [1, 3, 16, 24].

2.4. Secondary Resources of Zinc and Lead

In the world, zinc and lead are generally produced from primary sulphide or other ores. However, as stated before, increasing demand of metals has necessitated recovering metals from secondary resources or extraction of metals from low-grade ores. In other words, secondary resources have become a very important source for zinc and lead, like other metals, due to depletion of high grade ores and increasing demand of these metals [2, 19].

Today, in the world, over 70% of zinc is produced from zinc mines and remaining from industrial wastes [4]. There are various secondary zinc wastes discarded in different metallurgical plants. For instance, zinc ash, flux skimming or zinc dross come from galvanizing industry and leach residue comes from zinc plants from which zinc is produced via leaching methods. Moreover, considerable amount of recoverable zinc is present in blast furnace and electric arc furnace dusts. These zinc wastes have different chemical compositions as seen from Table 2.7 [2].

Table 2.7: List of Secondary Zinc Resources [2]

| | Types | Composition in wt % |
|----------------------------|---------------|--|
| Galvanizing Industry | Zinc Ash | 60-85 Zn, 0.3-2 Pb, 0.2-1.5 Fe, 2-12 Cl |
| | Flux Skimming | 5.6 metallic Zn, 48.1 ZnCl ₂ , 27.4 ZnO, 3.2 Al |
| | Zinc Dross | 96 Zn, 4 Fe |
| Electric Arc Furnace (AEF) | Dust | 19.4 Zn, 24.6 Fe, 4.5 Pb, 0.42 Cu, 1.4 Si, 6.8 Cl |
| Blast Furnace (BF) | Flue Dust | Major component Fe, also contains Zn, Si, Mg |
| Leaching Process | Leach Residue | 10-12 Zn, 15-17 Pb, 6-7 Fe, 8-10 CaO, 15-16 SiO ₂ |

On the other hand, lead is recovered from secondary resources which are based on mainly lead-acid batteries, and low amount zinc plant residues (neutral leach residue) and others. By the year 2000, more than 60 percent of the industry's production came from recycled materials, primarily due to the large number of scrapped lead batteries. Besides, in the last years recycling level of lead reached up to 83% of total consumption in USA [16].

2.5. Previous Studies on Leach Residues

2.5.1. Previous Studies on Recovery of Zinc and Lead from Çinkur Leach Residue

In this part, the previous studies about Çinkur leach residue will be given in chronological order. A number of studies have been carried out by researchers about Çinkur leach residue obtained from its discarded stock area. However, none of them have developed a feasible or applicable process for this residue.

First study about this topic was performed by the Mountain State Research and Development Co. [26] in 1977. This company conducted several heavy media separation tests on zinc-lead ores and leach residues by using flotation techniques. However, no success was achieved in producing a lead-zinc concentrate or in separating the lead and zinc contents of the leach residues. According to their

results, at least three factors were adversely influencing the recovery of the zinc in metallurgical treatment. These were:

- The smithsonite was intergrown with impure calcite,
- The hemimorphite which was a silicate compound in the ore did not float along with smithsonite,
- Some particles of these minerals were impregnated with iron oxide,

In 1979, a report was presented by SNC Services Ltd. [27] on the applicability of potential residue upgrading methods of both beneficiation and hydrometallurgical processing. In this report, it was recommended that Vieille Montagne beneficiation method could be applicable for Çinkur leach residue. In addition, three iron removal processes (Jarosite, Goethite and Hematite) were reviewed in detail and jarosite process was suggested due to the lower capital cost.

Kahraman et. al. [28] investigated the optimum sulphuric acid leaching conditions to reach maximum zinc recovery from Çinkur leach residue. After all trials, acid leaching conditions were determined as 5 M acid concentration, 40°C leaching temperature, 1/10 solid to liquid ratio and 4 h reaction duration. At these conditions 47% Zn recovery was achieved at the same time 53% Fe was dissolved. It was stated that Fe dissolution sharply increased with the increasing reaction temperature so the optimum leaching temperature was chosen as 40°C.

In addition to acid leaching process, chloride based leaching conditions were also investigated for Çinkur leach residue. Complex chloride solution was used to dissolve valuable metals in the residue. For this purpose, 1 M FeCl₃, 200 g/l NaCl and 10 g/l HCl were mixed and used for the residue at 100°C in 2 h. It was reported that 52% Zn and 87% Pb were recovered by applying chloride leaching.

Doğan et. al. [29] carried out some physical beneficiation methods to enrich zinc and lead in the leach residue. Initially, mineralogical leach residue analyses were done and it was found that leach residue was composed of PbSO₄, CaSO₄.2H₂O, ZnSO₄.H₂O, Fe₂O₃, ZnFe₂O₄, SiO₂ and other minor complex silicate compounds. In order to increase lead content in the leach residue, slime table, flotation and acid

leaching methods were used. By applying slime table method, lead content in the residue was improved from 19.7% to 27.2% with 47% recovery. On the other hand, in flotation method several reagents such as Na_2S , xanthate, pine oil were tried to increase lead content in the residue but lead in the final residue was never beyond 25.3%. Lastly, acid leaching method was applied to the leaching residue and the lead content in the final residue was about 31% after removal of zinc and iron in the residue.

Another study about metallurgical evaluation of Çinkur neutral leach residue was performed by the researchers of Istanbul Technical University [30]. Firstly, they have leached the residue with water in order to determine water soluble compounds. It was found that the residue contained notable amount of zinc and cadmium as ZnSO_4 and CdSO_4 . After that, acid leaching process was applied at different temperatures for various times in order to obtain maximum Zn recovery from the residue. By acid leaching practice, about 60% Zn recovery was obtained but 43% Fe was also dissolved. In order to remove iron in solution, jarosite process was suggested. In addition, it was considered that lead in the residue obtained after acid leaching could be enriched by using flotation method. However, this attempt was not successful.

Addemir [31] studied the metallurgical evaluation of Çinkur neutral leach residue by baking in concentrated sulphuric acid. This alternative study had two main steps. One was baking step starting from 150-250°C after mixing residue and sulphuric acid at predefined ratio. In this step, compounds zinc ferrite and iron oxide in the residue transformed to water soluble compounds zinc sulphate and iron sulphate. In the second step, residue obtained in the first step was heated to 600-650°C in order to convert $\text{Fe}_2(\text{SO}_4)_3$ to Fe_2O_3 . This baked cake was leached with water and over 90% zinc recovery was obtained. In addition, at the end of this process iron dissolution was very low (around 7%) because it was obtained as hematite which is not hazardous for the environment.

In 1992, a preliminary evaluation of pyrometallurgical processes was conducted by Cominco Engineering Service Ltd. (CESL) [25] in order to select a

pyrometallurgical process for treatment of Çinkur leach residue and ores. Four lead smelter processes namely Ausmelt, Kaldo, Kivcet and Outokumpu, for process characteristics such as metallurgy, commercial application, operating flexibility/versatility and simplicity were evaluated by CESL. After comparison of these processes, Kaldo was chosen as the recommended process for Çinkur leach residue and ores. However, this recommendation was never applied to treat either Çinkur ores or leach residues.

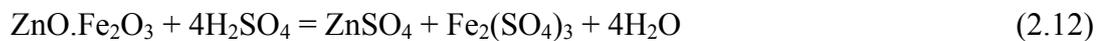
Most recent study about Çinkur leach residue was done by Turan et al. [32] in 2004. They have investigated zinc and lead recovery from zinc plant residue (ZPR) which was discarded as a cake from a Waelz kiln processing zinc-lead carbonate ores. Firstly, in order to recover zinc from residue, water leaching was performed at 25°C for 60 min. with a pulp density of 20% solids after roasting with an equal weight ratio of H₂SO₄/ZPR. They noted that roasting step after mixing ZPR with H₂SO₄ was needed to decompose the ferrite structure thus high zinc recovery could be obtained and they stated that about 85% zinc recovery could be obtained after roasting at 200°C for 30 minutes. Second step was carried out to recover lead from the secondary leach residue. In this step, secondary leach residue obtained after the first step was subjected to NaCl leaching. Their investigation showed that the recovery of lead significantly depended on NaCl concentration and pulp density. At the end of experiments, about 89% Pb was recovered in 200 g/l NaCl at 25°C in 10 minutes at a low pulp density (20 g/l). In addition, they recommended that lead from the second stage leach solution could be recovered by Na₂S precipitation in order to obtain a rich PbS concentrate which is suitable for pyrometallurgical treatment.

2.5.2. Previous Studies on Recovery of Zinc and Lead from Other Residues

There are a lot of recovery techniques of zinc and lead from secondary resources especially leaching residues. Generally, for this purpose hydrometallurgical method is the most convenient. In hydrometallurgical processes, different leachants are used for the recovery of zinc and lead.

Jha et. al. [2] reviewed in an article about the hydrometallurgical zinc recovery from industrial wastes. They described that various leachants could be used to recover zinc from secondary resources. According to this review paper, in all of the reagents, sulphuric acid is the best leachant to recover zinc from leach residues. Others are based on chloride (HCl, CaCl₂, etc.), ammonium (NH₄CO₃, NH₄Cl, etc.) and caustic soda (NaOH). Although some of them (sulphuric acid, ammonical solutions) have found commercial use in plants, the remaining processes are not applicable industrially due to insufficient recoveries or high costs.

As stated and approved by many researchers, sulphuric acid has been employed mostly for the hydrometallurgical extraction of zinc from ores or secondary resources since zinc oxide (ZnO) and zinc ferrite (ZnO.Fe₂O₃) being the most important compounds are soluble in concentrated sulphuric acid. Actually, zinc oxide can be dissolved even with dilute sulphuric acid but not zinc ferrite. Zinc oxide and zinc ferrite react with sulphuric acid according to the following reactions (2.11, 2.12) [9]:

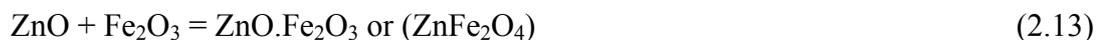


According to Jha et. al., [2] the Warren Spring Laboratory in UK carried out sulphuric acid leaching of EAF dust having 36% Zn as zinc ferrite and zinc oxide and reached 85 to 90% Zn recovery at pH 2 and 80% Zn recovery at pH 3 to 4 at 90°C.

By using acidic leach process, the recovery of zinc from slag which contained considerable amounts of zinc was investigated by Kurama and Göktepe [33]. In order to increase the recovery, leaching tests were performed in two stages in dilute and then concentrate sulphuric acid. Concentrated hot acid leaching step was applied to dissolve zinc ferrite present in the slag. It was found that about 77% Zn extraction could be achieved by atmospheric leaching.

As mentioned earlier, at hot acid leaching conditions, zinc ferrite dissolves and so zinc and iron are present in the leach solution. Zinc ferrite is the main source of iron

which is an undesirable element in the leach solution. In the commercial flowsheet for the zinc production during roasting stage, zinc ferrite forms at above 650°C according to reaction (2.13) between zinc and iron oxides present in the concentrate.



Since zinc ferrite is insoluble under normal leaching conditions with dilute sulphuric acid, its formation limits the zinc recovery of the processes. This is a problem only in processes operated with dilute sulphuric acid leaching. It has long been known that at the boiling point zinc ferrite dissolves in sulphuric acid. Zinc sulphate solution obtained by dissolving zinc ferrite contains high amount of iron as ferric sulphate which must be removed before electrolysis [34].

Iron is usually present in leach solutions and its elimination is a major operational problem in zinc hydrometallurgy. The removal of iron from such solutions is usually carried out by precipitation as jarosite, goethite or hematite.

The conventional jarosite process was developed and patented simultaneously by three different companies in early 1960s. In jarosite process, iron is precipitated from the hot acid leaching solution at elevated temperatures (95-97°C) in the presence of mainly Na^+ or NH_4^+ ions. Jarosites are complex basic iron sulphates, and their formation is represented by the following reaction (2.14) [35]:



where M represents any of the ions Na^+ , NH_4^+ , H_3O^+ , Li^+ , K^+ , $1/2\text{Pb}^{2+}$. According to Acharya et. al., [36] efficiency of the cations for iron removal in jarosite process was in the following order; $\text{Na}^+ > \text{NH}_4^+ > \text{K}^+$.

It was the first iron removal process and is still the most widely used process in the zinc industry today due to the production of a filterable iron residue on a commercial scale [37]. However, storage of the residue is a big problem since large amounts of residues are produced, and so this process has become questionable on environmental grounds [35].

The goethite process was developed by the Societe de la Viella Montagne in Belgium, in 1968 [37]. This process is successfully practiced in the electrolytic zinc industry. Iron is precipitated as goethite (FeO.OH) from an aqueous solution. This can be accomplished by reducing all ferric ions to the ferrous state or by adding the concentrated ferric solution to the precipitation tank at the same rate of goethite precipitation. The goethite is precipitated by reaction (2.15):



This reaction should be performed at 80–90°C and pH 2–3. It is necessary to neutralize the acid formed during the goethite precipitation. One advantage of precipitating iron as goethite instead of jarosite is the low volume of the waste goethite [35].

Another iron removal process called Hematite or Akita process was developed by Dowa Mining Company, Japan. This process contains mainly four steps:

- Leaching the residue with spent electrolyte and SO₂ gas,
- Precipitation of copper with H₂S gas,
- Neutralization of excess H₂SO₄ with lime,
- Conversion of iron to ferric state with oxygen [34].

In the first step, zinc leach residue is leached with a mixture of the spent acid in an autoclave operating at 95-100°C. After copper precipitation, solution is neutralized with addition of lime. In the last stage, solution is heated to around 200°C in titanium autoclaves and iron is precipitated as ferric oxide in oxygen atmosphere ($\rho\text{O}_2 > 5$ bar). The hydrolysis of ferrous sulphate to hematite is represented by the following reaction (2.16) [35]:



Hematite as a marketable material can be used in cement manufacture or pigments. Moreover, a high purity hematite (totally free of the contaminants) can be utilized in steel manufacture [38].

Apart from these three iron removal processes, some other processes have been investigated by researchers but not all of them can be used industrially due to various reasons essentially from economic point of view. Nonetheless, some (E.Z. process, conversion process, paragoethite process etc.) have been applied on a larger scale [34].

Although it is known that most important leachant is sulphuric acid in order to dissolve zinc ferrite, different leachants were examined by some researchers. Caustic soda (NaOH) is an example for these studies. Youcai and Stanforth [39] cited that zinc ferrite can be extracted after being fused directly with NaOH pellets and dissolved in an alkaline leaching solution. They studied with electric arc furnace dust which included high amount of zinc ferrite. By using magnetic separator, dust was separated into two fractions, and then magnetic fraction, primarily zinc ferrite, was leached in 11 M NaOH solution for 4 hours at 95°C. Other fraction, non-magnetic including mainly ZnO, was leached with 6 M NaOH solution for 1.5 hour at 95°C. They stated that at the end of these trials, over 80% of the total Zn and Pb recovery was obtained.

Youcai and Stanforth [40] studied caustic leaching about of EAF dusts and also smithsonite containing Zn-Pb ores. They proposed that ores should be broken into particles smaller than 0.1-0.5 mm and leached with 5 M NaOH solution at a 90-95°C temperature for 1.5 h. After filtration, the leach solution was reacted with sodium sulphide to separate lead as PbS and then sent to electrolysis process for the production of metallic Zn. They reported that over 85% of both Zn and Pb could be recovered at this leaching condition.

Another caustic soda leach technique was used by Xia and Pickles [41]. Unlike above technique, firstly dust was roasted with caustic soda at low temperatures. Therefore, zinc ferrite in the dust was converted into sodium zincate (Na₂ZnO₂) and iron oxide (Fe₂O₃) as seen in reaction (2.17).



After caustic roasting at about 400-450°C, dilute caustic leaching process was performed to recover zinc and lead. According to their results, about 95% Zn and 85% Pb were recovered and also the majority of iron oxide remained in the leach residue.

Lin Min [10] also tried to separate zinc and lead from industry wastes by using alkaline leaching. He used 5 M NaOH as the leaching reagent. After NaOH leaching at 25°C for 42 hours, only about 53% Zn and over 70% Pb could be recovered from the dust. Lead in the solution could be removed successively as lead sulphide (PbS) by the addition of solid sodium sulphide. Lead sulphide could be used directly in the lead smelters due to the presence of high amount lead content.

In addition to these processes, Blanco et. al. [42] studied the leaching behavior of zinc residue when using ammonium carbonate – ammonia solution. They developed an equation for the dissolution of zinc as a function of temperature, pH and solids concentration. Considering the equation, the optimum leaching parameters to achieve maximum zinc recovery should be as follows;

- Temperature as high as possible but less than boiling point of the solution.
- pH as high as possible. (Maximum pH limit 11 since ammonia solution was buffer solution)
- Solids concentration used will determine the capacity of the process.

It was stated that the maximum zinc recovery that could be obtained was 95% for zinc waste materials.

Chloride based processes were also used in hydrometallurgical processing of secondary residues containing zinc. HCl is one of the reagents for chlorination process. Nunez and Vinals [43] leached the residue containing zinc ferrite with hydrochloric acid and obtained zinc chloride ($ZnCl_2$). In addition, they investigated kinetics of zinc ferrite dissolution in aqueous hydrochloric acid solutions.

Ammonium chloride solution has also been used for the recovery of zinc from secondary resources. For this purpose, Ezinex process has been developed by

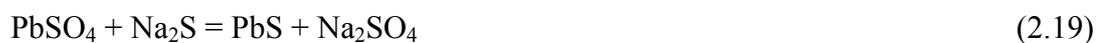
Engitec Implant. Olper et. al. [44] explained that this process was operated at 70-80°C for 1 hour and main leaching reaction was between zinc oxide and ammonium chloride in accordance with reaction (2.18)



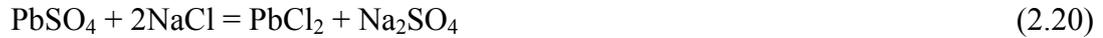
For recovery of lead from zinc plant residue several methods have been developed. For example, conversion of lead sulphate in residue to lead chloride (PbCl_2) by leaching with sodium chloride (NaCl) or lead hydroxide, ($\text{Pb}(\text{OH})_2$) by leaching with sodium hydroxide (NaOH) or lead carbonate (PbCO_3) by leaching with sodium carbonate (Na_2CO_3) has been investigated in lead recovery. According to Abdollahi et. al. [45] considering these three methods, NaCl (brine) can be selected as the most suitable leachant due to the low cost of salt without requirement of additional investment and any threat to the environment.

Raghavan et. al. [46] stated that sulphuric acid leaching was performed to dissolve zinc and so lead will be enriched in the residue. The residue was treated with brine (NaCl) solution to solubilise most of the lead. They have developed a hydrometallurgical process convenient with this procedure. Firstly, they leached the residue with sulphuric acid (200 g/l) at 85°C for 2 h and continued with brine leaching, 300 g/l NaCl , for 30 min at pH 1.5-2. In addition, they tried to cement out lead by using zinc, iron or aluminum. At the end of all these trials they recovered around 90% Pb and 80% Zn.

In a more recent work reported by Raghavan et. al. [47], it was tried to transform PbSO_4 to PbS by using sodium sulphide (Na_2S) and sodium chloride (NaCl). They proposed two methods in order to produce high quality lead concentrate. First part of the work was concerned with a double decomposition technique; to remove acid soluble metals, the residue was leached with dilute sulphuric acid and to convert PbSO_4 into PbS with Na_2S after the first step treatment. Conversion reaction (2.19) occurs between PbSO_4 and Na_2S as follows:

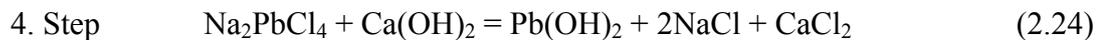
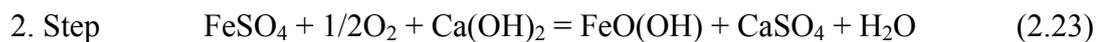


In the second method, they leached the residue with NaCl to produce PbCl₂ and then subjected to Na₂S to obtain PbS. The main leaching reactions (2.20 and 2.21) were written by Raghavan as follows:

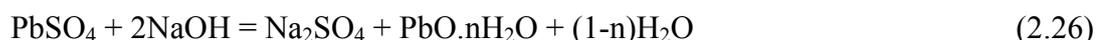


They claimed that sodium chloride was a good reagent for lead sulphate and at the end of process the same amount of NaCl was regenerated by the addition of sodium sulphide.

PLINT is also a chloride base technology able to deal with many different feed materials. It is a simplified version of the original PLACID process developed by Tecnicas Reunidas (TR) for lead extraction from recycled lead-acid batteries. The PLINT process is based on hot brine closed loop circuit that contains four main steps. First step is leaching of the feed materials to dissolve valuable metals in chloride media. In second step, iron and sulphate are removed by addition of lime. Next step is recovery of precious metal (Au, Ag) by cementation with a less noble metal powder such as Fe, Zn or Pb. Lastly, lead is recovered in the form of lead carbonate or pure lead oxide concentrate that could be used at a lead secondary plant. Reactions (2.22 - 2.25) are given as follows [48]:



Another lead-acid battery recycling process was described by Olper [49]. It was reported that NaOH or Na₂CO₃ could be used for desulphurization as seen from the following reactions (2.26 and 2.27):



It was also stated that use of sodium hydroxide versus sodium carbonate should be carefully determined. By using a 50% sodium hydroxide solution, desulphurization reaction was completed 95%.

Arai and Togurai [50] also examined lead recovery from lead acid battery with treatment of sodium carbonate. It was claimed that the conversion rate for the carbonate leaching of lead sulphate in Na₂CO₃ solution was greatly affected by the concentration of the carbonate ions. According to their experimental results, under the optimum leaching conditions, lead carbonate recovery of 98% could be obtained in less than 30 minutes at room temperature.

Apart from all these methods mentioned above, for lead recovery ammonium sulphate, calcium chloride, and diethylenetriamine (DETA) were also used as reagents by some researchers. For example, Guy et. al. [51] studied solubility of lead and zinc compounds in ammonical ammonium sulphate (AAS) solutions. It was stated that large concentrations of AAS solution enhance the lead solubility.

It is noteworthy that 99.5% Pb extraction was achieved by Kalashnikova et. al. [52] at the optimal chloride leaching conditions. They reported that major part of the lead passes to the solution according to reaction (2.28):



On the other hand, Ek C.S. [53] tried to recover lead and silver from hydrometallurgical zinc residues. Firstly, a super hot acid leaching process was applied to dissolve other metals except for lead and silver. Then, to obtain lead and silver several tests were carried out with DETA at room temperature for 2 h. It was stated that after performing the tests, lead could be recovered as a pure carbonate by blowing CO₂ into the solution. In addition it was stated that DETA is an excellent leaching reagent for PbSO₄ due to the production of a pure lead carbonate.

CHAPTER III

EXPERIMENTAL PART

3.1. Introduction

In this chapter, initially, the materials used during this study will be explained. Then, physical, chemical and mineralogical characterizations of the leach residues will be given. Lastly, the experimental set-up and procedure of water, acid and also brine leaching experiments will be described.

3.2. Materials

Çinkur is the only plant in Turkey that produces zinc from primary ore containing zinc carbonate. In order to realize zinc production, it was constructed in 1976 in Kayseri. This factory was operated from its establishment until 1997 by using primary zinc-lead carbonate ores. After this year, zinc concentrate coming from Iran was used until this plant was shut down in 2000 due to financial difficulties and depletion of high grade ores. Therefore, there are two different leach residues (LR), namely Turkish and Iranian, in Çinkur stockpiles. Turkish leach residue (TLR) was produced by processing of Turkish zinc and lead carbonate ores and there is approximately 900,000 tons of it. On the other hand, Iranian leach residue (ILR) was produced by processing imported Iranian zinc concentrate and there is approximately 100,000 tons of this leach residue in the stockpile. Recently, due to rising prices of metals Çinkur started to process mainly electric arc furnace dust and is producing clinkers containing zinc and lead for export.

In the year 2003, Turkish LR and Iranian LR were obtained from Çinkur stockpiles by the help of a retired Çinkur engineer. After obtaining the residues, each one was dried at 105°C then, put through a disc pulverizer in order to disperse the sticking fine particles and used for this thesis study.

In this study, according to their weight ratio of residues in the stockyard blended leach residue (BLR) was prepared as the starting material by mixing 9 parts of Turkish leach residue and 1 part of Iranian leach residue. This mixture was used in all of the experiments.

3.3. Characterization of the Materials

In characterization of the materials, firstly the physical characterizations of Turkish, Iranian and blended leach residues were done to determine their moisture content, particle size, bulk density and specific gravity after each sample was homogenously mixed, dried and pulverized. Residues were also analyzed chemically to find out their chemical compositions by using Atomic Absorption Spectrophotometer (AAS) and X-Ray Fluorescence (XRF). Then, the mineralogical characterizations of each sample and the blend were done by X-Ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). At last, Thermal Gravimetric Analysis (TGA) of blended LR was done to investigate the thermal behavior of the sample. Results of analyses mentioned above will be given in the following sections.

3.3.1. Moisture Content Measurements

Moisture contents of Turkish and Iranian leach residues were determined by drying the representative samples in a drying oven. Results of their moisture contents are given in Table 3.1.

From these results, it was concluded that Turkish LR and Iranian LR had 4.8% and 3.5% moisture, respectively. However, as mentioned above, since these residues had been dried at 105°C before in 2003, moisture contents of the residues were very low compared to initial residues coming from Çinkur stockyard. The stated moisture contents were picked up from the atmosphere during their long period of

storage in the laboratory. The original moisture contents of Turkish and Iranian leach residues were found as 19.5% and 30.9%, respectively [7].

Table 3.1: Moisture contents of Turkish LR and Iranian Leach Residues

| Sample | Initial weight (g) | Final weight (g) | Difference (g) | % Moisture |
|------------|--------------------|------------------|----------------|------------|
| Turkish LR | 1000 | 952 | 48 | 4.80 |
| Iranian LR | 1000 | 965 | 35 | 3.50 |

3.3.2. Bulk Density and Specific Gravity Determinations

To determine its bulk density each residue was filled in a 1 liter measuring cylinder and weighed with tare. In addition, specific gravity of each leach residue was determined by using a water pycnometer at the Department of Metallurgical and Materials Engineering of METU and the specific gravity of blended leach residue was also determined with helium pycnometer at the Central Laboratory of METU. Bulk densities and specific gravities of the leach residues are given in Tables 3.2 and 3.3. In summary, the bulk density of blended LR was found as 0.94 g/cm³ and the specific gravity of blended LR was determined as 3.46 by water pycnometer and 3.62 by He pycnometer.

Table 3.2: Bulk Density and Specific Gravity of Turkish, Iranian and Blended Leach Residues

| Sample | Bulk Density (g/cm ³) | Specific Gravity by Water Pycnometer |
|------------|-----------------------------------|--------------------------------------|
| Turkish LR | 0.97 | 3.28 |
| Iranian LR | 0.77 | 3.69 |
| Blended LR | 0.94 | 3.46 |

When the specific gravity of blended LR in Table 3.2 is compared to the specific gravity of blended LR in Table 3.3, the value measured by water pycnometer is lower than that determined by He pycnometer. This was due to the presence of soluble compounds such as $ZnSO_4 \cdot 7H_2O$ in blended LR.

Table 3.3: Specific Gravity of Blended LR by Helium Pycnometer

| Sample | Temperature (°C) | Specific Gravity |
|-----------------------|------------------|------------------|
| Blended Leach Residue | 25 | 3.62 |

3.3.3. Screen Analysis

Particle size of blended LR and its distribution were determined by wet screen analysis method. Result of wet screen analysis is given in Table 3.4.

According to the wet sieve analysis of the sample, as seen in Table 3.4, about 76% of the residue was under 100 μm . Moreover, calculations showed that blended LR dissolved in water approximately by 8.4%.

Table 3.4: Wet Screen Analysis of Blended LR

| Particle Size (Micron) | Weight (%) | Cumulative Weight % Oversize | Cumulative Weight % Undersize |
|------------------------|------------|------------------------------|-------------------------------|
| 300 | 4.58 | 4.58 | 95.42 |
| 212 | 5.96 | 10.54 | 89.46 |
| 150 | 6.16 | 16.70 | 83.30 |
| 106 | 7.22 | 23.92 | 76.08 |
| 75 | 2.34 | 26.26 | 73.74 |
| 53 | 3.32 | 29.58 | 70.42 |
| 38 | 4.66 | 34.24 | 65.76 |
| Pan | 57.40 | - | - |
| TOTAL | 91.64 | % 8.36 dissolution in water | |

3.3.4. Chemical Analysis

Chemical analyses of Turkish, Iranian and blended leach residues were carried out by Atomic Absorption Spectrophotometer in the Department of Metallurgical and Materials Engineering Chemistry Laboratory. Using the Atomic Absorption Spectrophotometer, only Zn, Pb and Fe contents of the samples were determined. In order to determine the other components of Turkish, Iranian and blended leach residues, X-Ray Fluorescence in the Department of Mining Engineering of METU was used. Table 3.5 summarizes the chemical analysis of Turkish, Iranian and blended leach residue results obtained after determination by AAS and XRF.

Table 3.5: Chemical Analysis Results of Turkish, Iranian and Blended Leach Residues

| Component | Turkish LR (wt %) | Iranian LR (wt %) | Blended LR (wt %) |
|--------------------------------|----------------------|----------------------|----------------------|
| Pb | 16.45 | 8.26 | 15.51 |
| Zn | 11.89 | 16.31 | 12.43 |
| Fe | 6.79 | 5.53 | 6.27 |
| Cd | 0.04 | 0.21 | 0.05 |
| SO ₃ | 19.72 | 22.50 | 20.48 |
| SiO ₂ | 15.86 | 20.11 | 17.18 |
| CaO | 8.50 | 4.19 | 7.57 |
| Al ₂ O ₃ | 3.91 | 6.58 | 3.99 |
| MnO | 0.58 | 1.71 | 0.79 |
| MgO | 0.95 | 1.29 | 0.98 |
| K ₂ O | 0.01 | 0.98 | 0.14 |
| BaO | 0.44 | 0.28 | 0.36 |

From the results, it was found that Zn, Pb and Fe contents of blended LR were 12.43%, 15.51% and 6.27%, respectively. In addition, from Table 3.5, it can be seen that the amounts of several elements or compounds such as Zn, SiO₂, Al₂O₃, MnO, MgO and K₂O in Iranian LR were higher than those in Turkish LR. On the other hand, Turkish LR contained more Pb, Fe, and CaO.

3.3.5. XRD Analysis

X-Ray Diffraction (XRD) was used in this study to analyze the mineral composition of Iranian, Turkish and blended leach residues. The peaks of diffraction were recorded and plotted against a horizontal scale in degrees of 2θ , which is the angle

of the detector rotation in order to catch the diffracted X-Ray. The XRD results of Turkish, Iranian and blended leach residues have been presented in Figures 3.1, 3.2 and 3.3, respectively.

In previous studies [32, 54] Çinkur leach residue was exposed to a series of selective zinc extraction tests and these tests indicated that zinc was present in the residue as sulphate, ferrite, silicate and complex oxide forms. Most of these phases can be also seen from the XRD results of all the leach residues. In XRD pattern of blended LR, lead sulphate (PbSO_4) and calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) were identified as major components. The others were identified as minor components. Although the peaks of major phases overlapped on peaks of minor phases, other compounds could be identified as iron silicate (Fe_2SiO_4), zinc ferrite (ZnFe_2O_4), zinc silicate (Zn_2SiO_4), zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), iron oxide (Fe_2O_3), calcium silicate (Ca_2SiO_4), and quartz (SiO_2).

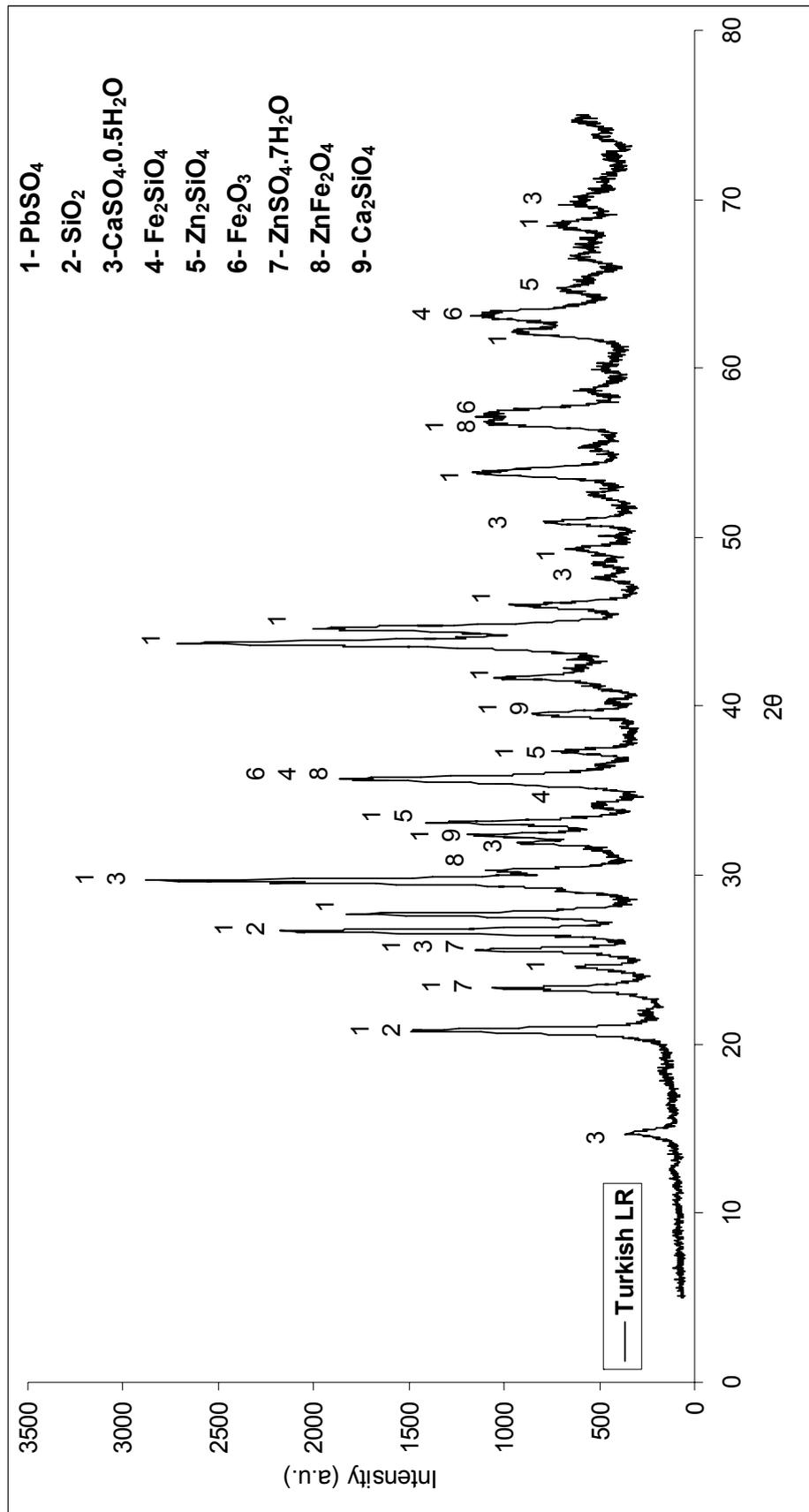


Figure 3.1: XRD Analysis of Turkish LR

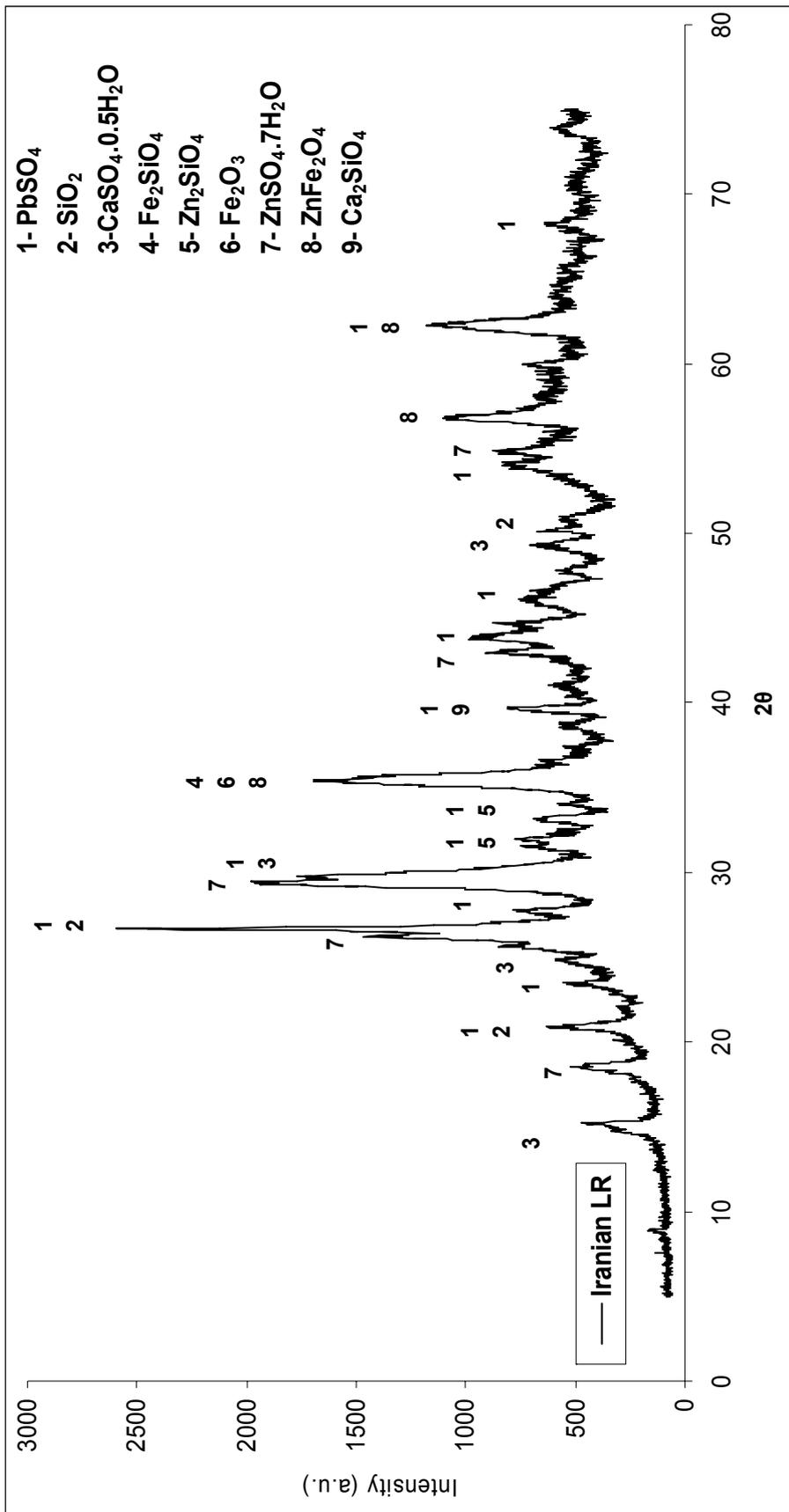


Figure 3.2: XRD Analysis of Iranian LR

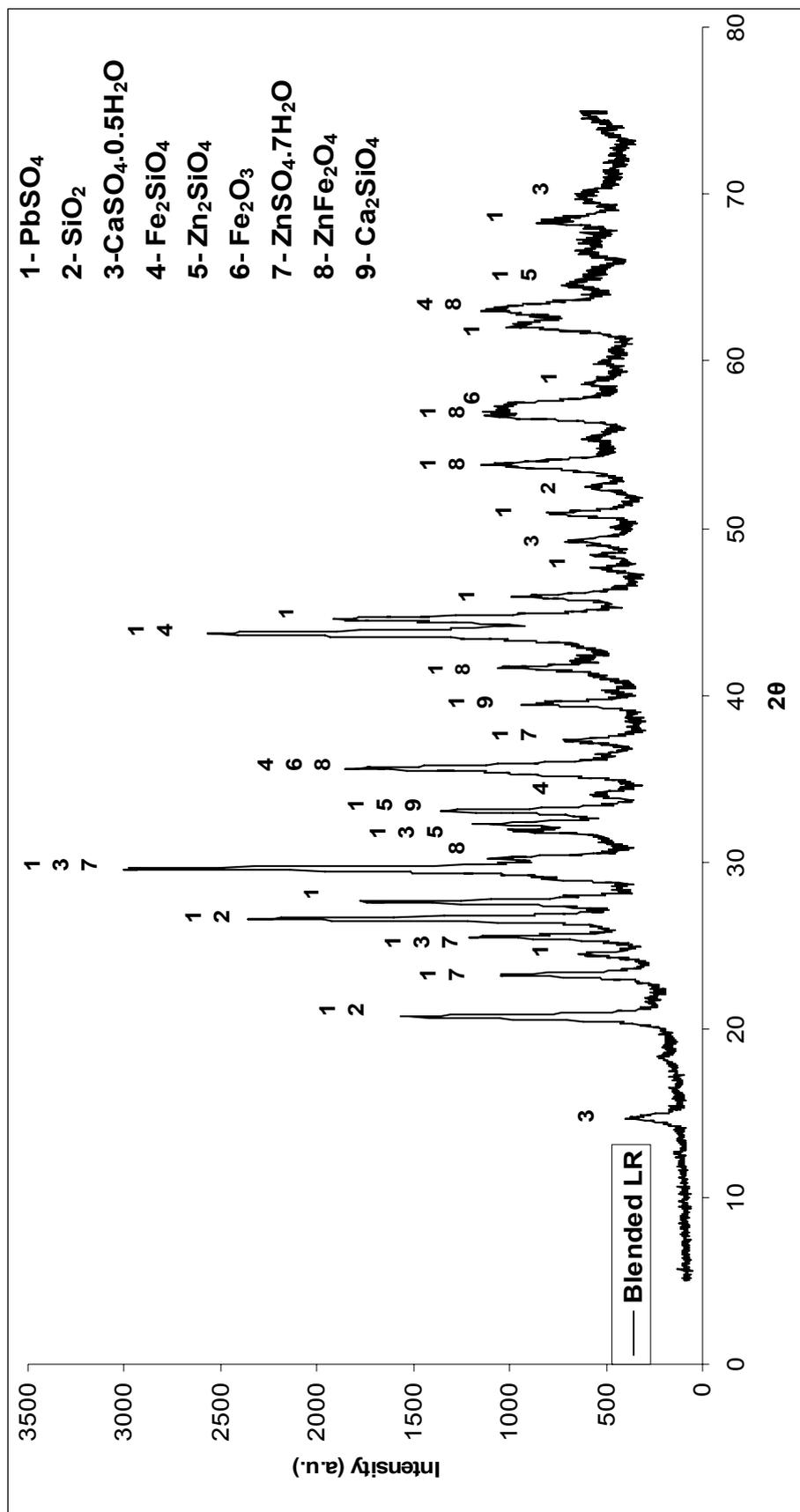


Figure 3.3: XRD Analysis of Blended LR

3.3.6. SEM Analysis

Although there are various compounds or phases present in the blended LR, Turkish LR and Iranian LR as seen in the XRF and XRD analyses of TLR, ILR and BLR, some of them could not be determined such as those including Al, Mg, K, etc. Therefore, in order to analyze these residues in detail, Scanning Electron Microscopy (SEM) studies were done on gold coated samples and for this purpose JEOL JMS 6400 type SEM equipped with EDS Tracor Series II analysis system available in the Metallurgical and Material Engineering Department was used. Bulk area analyses for Turkish, Iranian and blended leach residues can be seen in Figures 3.4, 3.5, and 3.6 and in Tables 3.6, 3.7, and 3.8, respectively.

In general, SEM analyses results of the residues showed parallelism with the results of XRF, AAS and XRD. Differently, the results of SEM analyses proved that some complex compounds including Al, Mg and K existed in the residues. Moreover, from EDS analysis of the residues (Tables 3.6 and 3.7) it can be seen that Al, Mg and K in Iranian LR were present more in amount as compared to Turkish LR.

Except for bulk area analyses of the residues, specific particle analyses were also done to identify different phases in the residues. These particle analyses helped us to detect and characterize the large particles such as SiO_2 , PbSO_4 , and $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ etc. in the residues. Due to the very fine particle size of the residues, all the phases could not be identified because of the resulting interference.

Full scale counts: 852

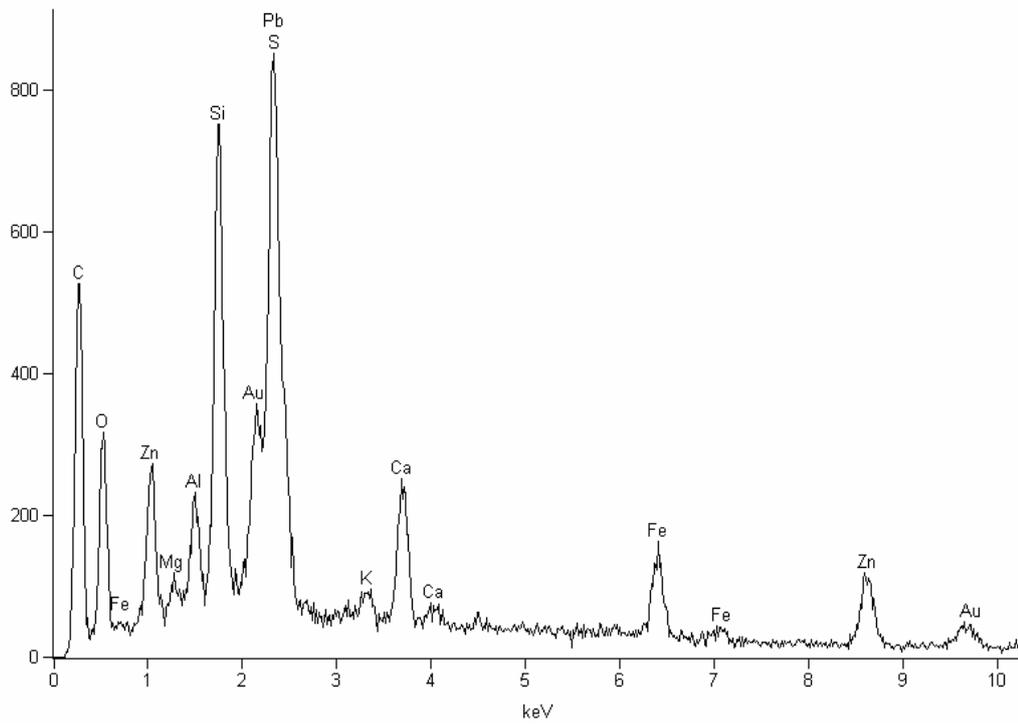


Figure 3.4: SEM Analysis of Turkish LR

Table 3.6: EDS Analysis of Turkish LR

| Element | Weight Concentration (%) | Atom Concentration (%) |
|---------|--------------------------|------------------------|
| Pb | 17.26 | 3.85 |
| Zn | 10.49 | 5.04 |
| Fe | 7.42 | 3.79 |
| O | 34.21 | 62.86 |
| S | 7.85 | 6.11 |
| Si | 7.66 | 7.92 |
| Ca | 6.59 | 5.47 |
| Al | 1.10 | 1.24 |
| K | 0.27 | 0.21 |
| Mg | 0.66 | 1.44 |

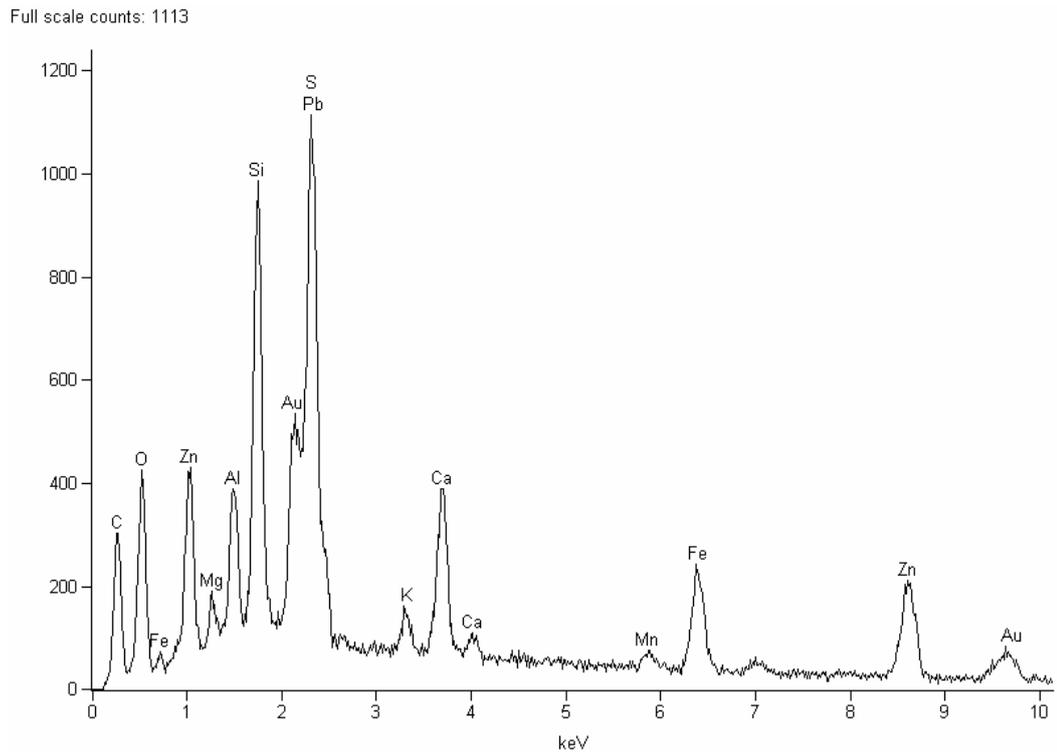


Figure 3.5: SEM Analysis of Iranian LR

Table 3.7: EDS Analysis of Iranian LR

| Element | Weight Concentration (%) | Atom Concentration (%) |
|---------|--------------------------|------------------------|
| Pb | 9.26 | 2.14 |
| Zn | 16.52 | 7.60 |
| Fe | 5.76 | 2.87 |
| O | 30.63 | 57.39 |
| S | 11.15 | 9.81 |
| Si | 9.49 | 9.77 |
| Ca | 3.82 | 2.98 |
| Al | 3.03 | 3.42 |
| K | 1.18 | 0.78 |
| Mg | 0.98 | 2.13 |

Full scale counts: 479

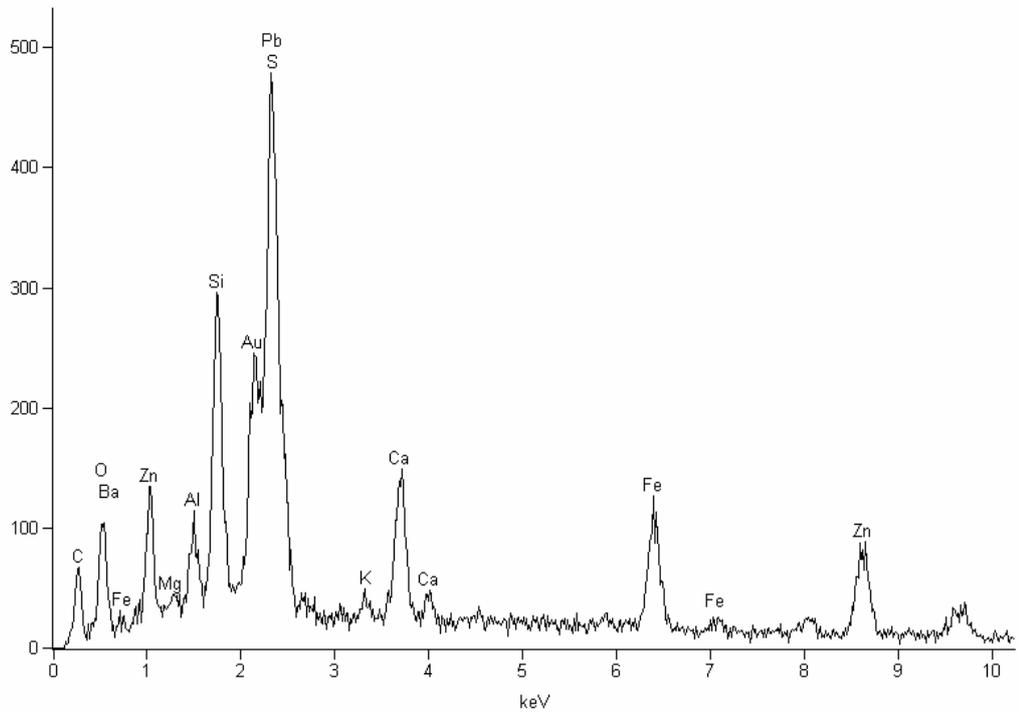


Figure 3.6: SEM Analysis of Blended LR

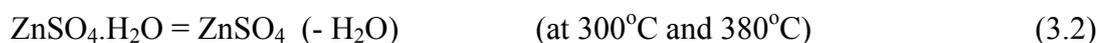
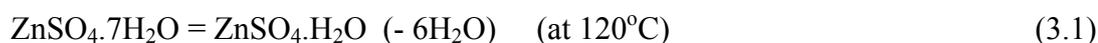
Table 3.8: EDS Analysis of Blended LR

| Element | Weight Concentration (%) | Atom Concentration (%) |
|---------|--------------------------|------------------------|
| Pb | 16.56 | 2.34 |
| Zn | 12.52 | 5.60 |
| Fe | 7.53 | 3.95 |
| O | 34.97 | 63.99 |
| S | 10.11 | 9.23 |
| Si | 6.49 | 6.77 |
| Ca | 4.82 | 3.52 |
| Al | 2.23 | 2.42 |
| K | 0.63 | 0.47 |

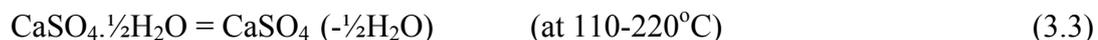
3.3.7. Thermal Analysis

Thermogravimetric analysis (TGA) was carried out to find out the thermal behavior of blended LR from 30°C to 980°C. 100 mg of blended LR sample was analyzed with a linear heating rate of 25°C/min in N₂ by the Central Laboratory at METU. Result of the thermogravimetric analysis is given in Figure 3.7.

Weight loss occurring during thermogravimetric analysis can be explained by evaporation of the chemically bonded water and several decompositions. Blended LR contains two compounds including chemically bonded water. These compounds are zinc sulphate heptahydrate (ZnSO₄.7H₂O) and calcium sulphate hemihydrate (CaSO₄.½H₂O). Dehydration of zinc sulphate heptahydrate initially occurs on heating to about 120°C. At this point, 6 moles of water is removed. On further heating, two new peaks are observed on the TGA curve at around 300°C and 380°C so 1 mole of water is lost at these temperatures [55]. Dehydration reactions (3.1, 3.2) occur as follow;



On the other hand, dehydration of calcium sulphate hemihydrate occurs approximately at the same temperatures with dehydration of zinc sulphate heptahydrate. During heating, dehydration of calcium sulphate hemihydrate (CaSO₄.½H₂O), also starts at 110°C and continues up to about 220°C. When the hemihydrate is heated further, anhydrite calcium sulphate (CaSO₄) forms according to following reaction (3.3) [56].



After the loss of water from the compounds, decomposition of zinc sulphate and decomposition of calcium sulphate occur at different temperatures. Desulphurization of anhydrous zinc sulphate (ZnSO₄) begins at about 600°C and ends at 930°C, so only ZnO remains in the residue [55]. On the other hand, in the

pure state anhydrite calcium sulphate does not show any thermal transformation until 1200°C [56]. Therefore, desulphurization of the calcium sulphate on the TGA curve is not observed.

As a result, the free moisture and chemically bonded water removal in $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ start at 110°C and these are completely removed until about 380°C. Above this temperature, there is no water in the residue. Then, desulphurization of the anhydrous sulphate begins at about 600°C. All these effects can be seen in Figure 3.7.

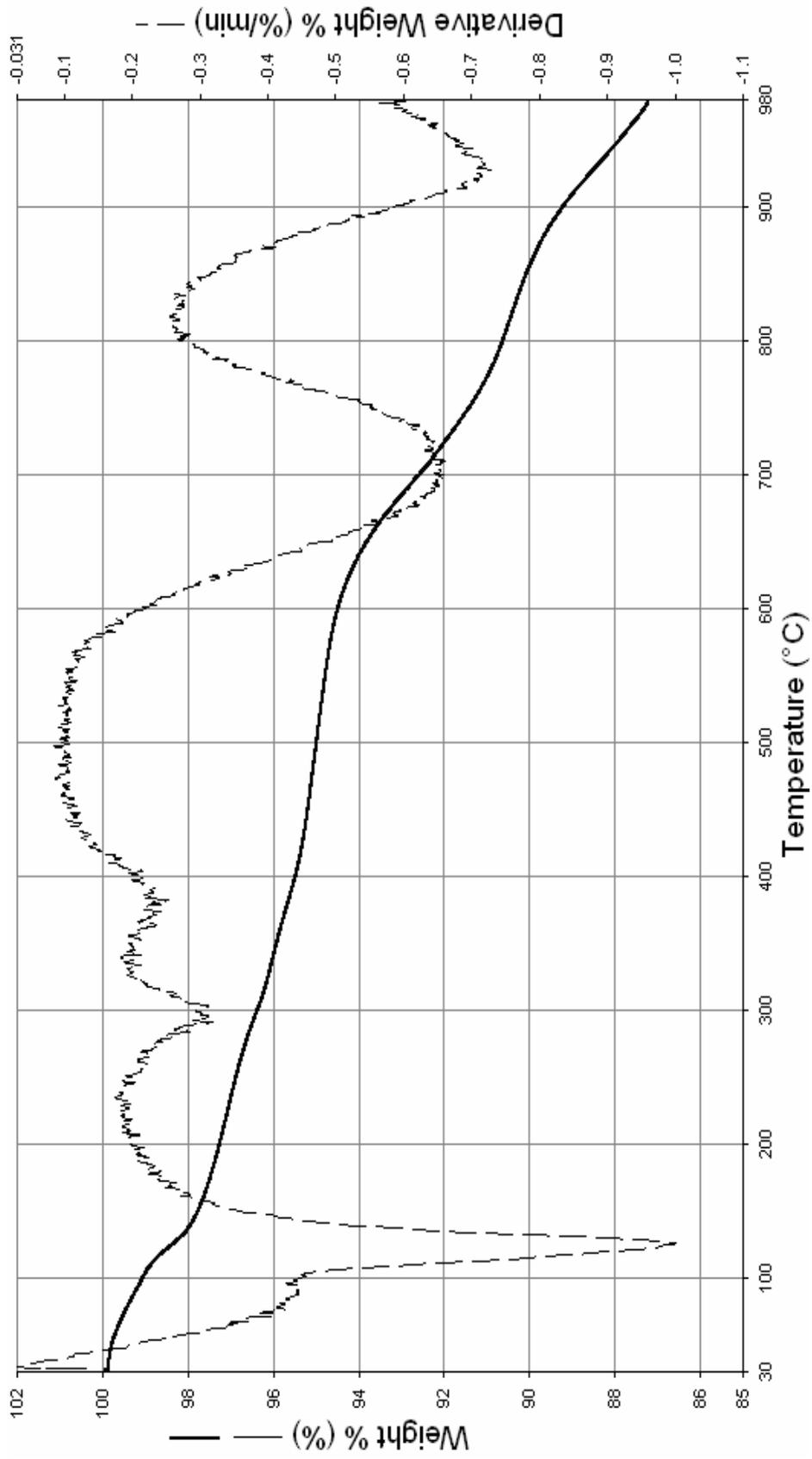


Figure 3.7: Thermogravimetric Analysis of Blended LR

3.4. Experimental Set-up and Procedure in Leaching Experiments

In the leaching experiments Velp Scientifica AREX2 model hot plate, Teflon coated magnetic stirrer and 250 ml Pyrex balloons with three necks were used as the experimental leaching equipment. Temperature was controlled by a contact thermometer having $\pm 1^\circ\text{C}$ sensitivity. In addition, a water cooled condenser was attached to the system to eliminate evaporation losses at high temperatures. During the experiments, the magnetic stirring speed was fixed at a constant value. Schematic drawing of the set-up is shown in Figure 3.8.

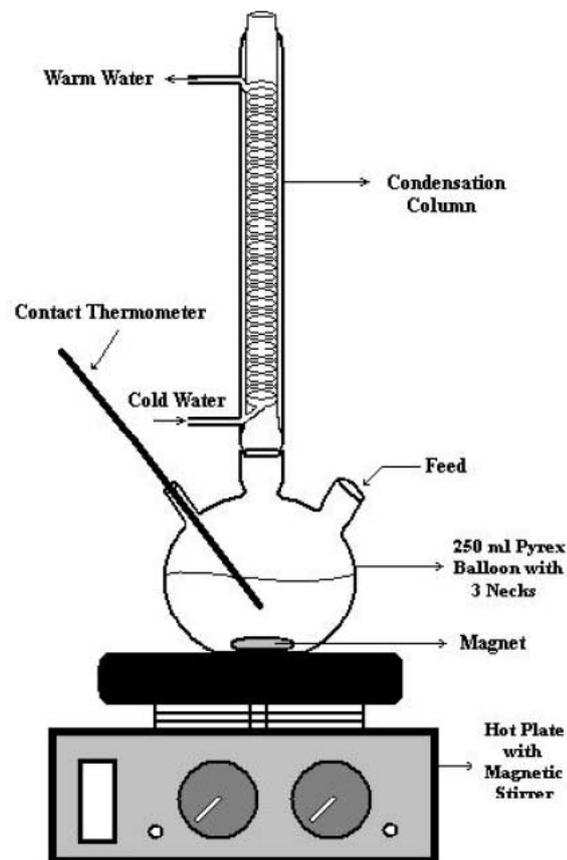


Figure 3.8: Experimental Set-up of Leaching

Leaching experiments were started with water leaching. These trials were performed only to determine water solubility of the residues. Reaction temperature and reaction duration were chosen in range of 25-95°C and 1-3 h, respectively.

In addition sulphuric acid leaching experiments were done to determine the recovery of zinc. Experimental variables were chosen as temperature (25-99°C), reaction duration (1-32 h), acid concentration (0-350 g/l) and solid to liquid ratio (pulp density) (1/4-1/6 g/cc).

At the last stage, secondary leach residue (SLR) obtained at the end of acid leaching trials was treated with brine solution for the recovery of lead. The effects of NaCl concentration (0-300g/l), solid to liquid ratio (1/4-1/40 g/cc), leaching temperature (25-102°C) and reaction duration (5-300 min.) were chosen as the experimental parameters.

Except for pulp density trials, all of the leaching experiments were carried out with 20 grams of blended LR or SLR and 100 ml volume solution which was composed of de-ionized water and predefined amount of leachant (sulphuric acid or sodium chloride). During all of these tests, de-ionized water, Merck quality sulphuric acid (95-98 wt%), hydrochloric acid (35 wt%) and sodium chloride (99.5 wt%) were used.

After each leaching experiment, the solution was filtered by a vacuum pump using S&S brand filter papers with blue band. Firstly, the filter paper was weighed and placed into a Buchner funnel. Then, leach solution was poured onto the filter paper carefully and slowly to separate pregnant leach solution from solid leach residue. Then, the solid sample remaining on the filter paper was washed with de-ionized water. After washing, solid residue with the filter paper was taken out of the Buchner funnel and was put onto a watch glass. Then, the watch glass was placed into a drying oven preheated to 105°C and kept there for about 3 hours. After drying, filter cake was weighed again to determine the weight of each leach residue and sent to the chemical laboratory for analyzing Zn, Pb and Fe by AAS. The obtained results were used to calculate leach recoveries of Zn, Fe and Pb.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Introduction

In order to determine the leachability of blended LR of Çinkur with water, sulphuric acid and brine under atmospheric pressure, a series of tests were carried out. In these tests, the effect of acid concentration, pulp density (solid/liquid ratio), reaction duration, leaching temperature and brine concentration as well as HCl additions were investigated. The results are presented in the following sections.

4.2. Water Leaching

Initial experiments were done with de-ionized water by using the experimental set-up given in Chapter III. In water leaching trials reaction duration (1-3 h) and reaction temperature (25-95°C) were selected as the parameters to be investigated. These leaching trials were performed to determine zinc recovery from blended LR in water.

In the thesis, recovery term was used to state the amount of metal which could be taken into the leach solution. For water, acid and brine leaching different recovery equations were used in order to calculate metal recovery. In the water leaching part, the recovery of zinc was calculated by using the following equation (4.1):

$$\%R_{Zn} = \left(\frac{W_{LR} * C_{LR} - W_{SLR} * C_{SLR}}{W_{LR} * C_{LR}} \right) * 100 \quad (4.1)$$

W_{LR} : Weight of initial leach residue in grams, W_{SLR} : Weight of secondary leach residue in grams, C_{LR} : Weight percent (Concentration) of metal (Zn) in initial leach residue, C_{SLR} : Weight percent (Concentration) of metal (Zn) in secondary leach residue.

4.2.1. Effect of Reaction Duration on Zinc Recovery in Water Leaching

During the experiments conducted for the determination of the effect of reaction duration, the other parameters were kept constant at solid/liquid ratio (1/5 g/cc) or pulp density of (200 g/l) and reaction temperature of 25°C. Results of the experiments are given in Table 4.1 and Figure 4.1.

Table 4.1: Effect of Reaction Duration on Zinc Recovery in Water Leaching

| Experimental Code | Reaction Duration (h) | Zn Recovery (%) |
|--|-----------------------|-----------------|
| SL-1 | 1 | 10.1 |
| SL-2 | 2 | 11.8 |
| SL-3 | 3 | 12.3 |
| Reaction Temperature: 25°C, Solid/Liquid Ratio: 1/5 g/cc | | |

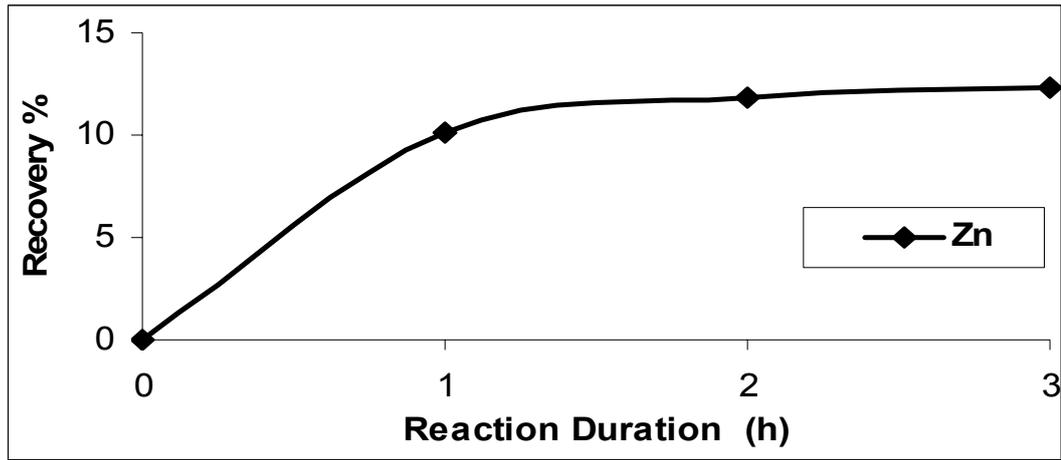


Figure 4.1: Effect of Reaction Duration on Zinc Recovery in Water Leaching.

From the results, it is seen that beyond 1 h of leaching duration, the increase in leach recovery of zinc was not substantial. As a result of this, it can be said that in one hour most of the zinc that was recoverable by water leaching from blended LR was taken into solution.

4.2.2. Effect of Reaction Temperature on Zinc Recovery in Water Leaching

Effect of temperature was investigated by choosing solid/liquid ratio as 1/5 g/cc and reaction duration as 1 h. Results of the trials are given in Table 4.2 and Figure 4.2.

Table 4.2: Effect of Reaction Temperature on Zinc Recovery in Water Leaching

| Experimental Code | Reaction Temperature (°C) | Zn Recovery (%) |
|--|---------------------------|-----------------|
| SL-1 | 25 | 10.1 |
| SL-4 | 45 | 14.8 |
| SL-5 | 95 | 18.4 |
| Reaction Duration: 1 h, Solid/Liquid Ratio: 1/5 g/cc | | |

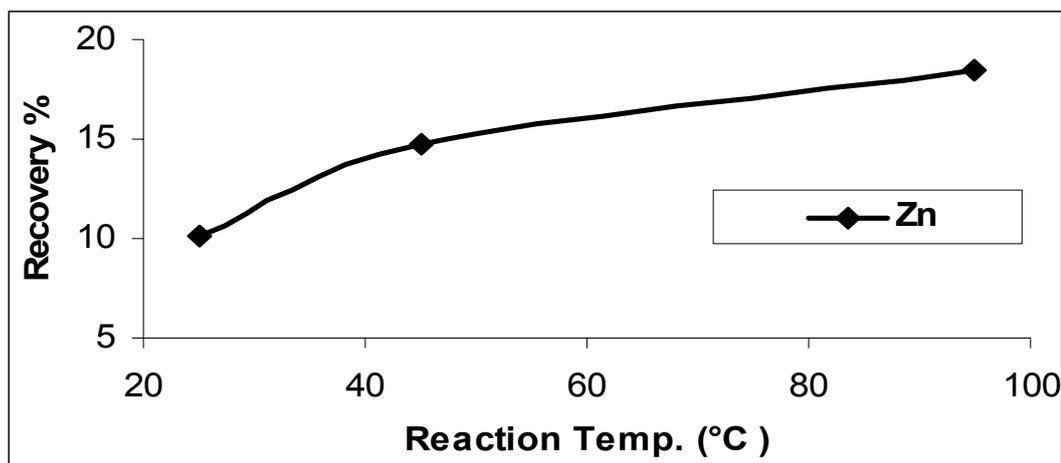


Figure 4.2: Effect of Reaction Temperature on Zinc Recovery in Water Leaching

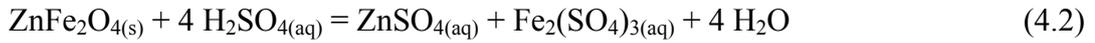
As it can be seen from these results, the recovery of zinc increased with the increasing reaction temperature and reached a maximum value at 95°C. Therefore, this value can be chosen as the optimum reaction temperature.

As mentioned before, blended LR contains many compounds including ZnFe_2O_4 , Zn_2SiO_4 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, PbSO_4 and others. However, in water leaching experiments, zinc recovery was restricted by the amount of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in blended LR, because only $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is soluble in water. In conclusion, it can be said that zinc recovery in water leaching increased with increasing reaction duration especially in the first hour and increasing reaction temperature. The maximum zinc recovery in water leaching experiments was found to be about 18% which was due to the presence of limited amount of zinc in blended LR as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. In the light of these results it was concluded that percentage of zinc originating from zinc heptahydrate was $(12.43 \cdot 18 / 100 = 2.23\%)$ 2.23% which corresponded to 9.85% $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ($2.23 \cdot 287 / 65 = 9.85\%$) in blended LR.

4.3. Acid Leaching

Due to insufficient zinc recoveries of water leaching tests and the presence of acid soluble compound such as zinc ferrite in the leach residues, acid leaching tests were done for zinc recovery. During acid leaching experiments, as a leachant, sulphuric

acid (H₂SO₄) solution was used. When the blended leach residue was subjected to sulphuric acid solution, zinc ferrite (ZnFe₂O₄) in the leach residue was converted to water soluble zinc sulphate (ZnSO₄) according to reaction (4.2) [57]. Other zinc forms, such as silicate and complex, in the blended LR did not react with sulphuric acid [1].



In acid leaching, variables chosen were acid concentration (0-350 g/l), reaction duration (1-32 h), reaction temperature (25-99°C), and solid/liquid ratio (1/4-1/6 g/cc). In the experiments, the recovery of zinc and dissolution of iron were calculated by using the following formula (4.3):

$$\%R_{\text{Zn,Fe}} = \left(\frac{W_{LR} * C_{LR} - W_{SLR} * C_{SLR}}{W_{LR} * C_{LR}} \right) * 100 \quad (4.3)$$

W_{LR} : Weight of initial leach residue in grams, W_{SLR} : Weight of secondary leach residue in grams, C_{LR} : Weight percent (Concentration) of metal (Zn or Fe) in initial leach residue, C_{SLR} : Weight percent (Concentration) of metal (Zn or Fe) in secondary leach residue.

4.3.1. Effect of H₂SO₄ Concentration on Zinc Recovery in Acid Leaching

In this study, blended LR was tested at five different levels of sulphuric acid concentrations, which were 50, 100, 150, 250 and 350 g/l. During the tests, the following parameters were kept constant: Solid/liquid ratio: 1/5 (g/cc); reaction duration: 1 hour; reaction temperature: 95°C.

Zinc recoveries with changing sulphuric acid concentration are given in Table 4.3 and Figure 4.3. Results showed that the concentration of sulphuric acid was a very important parameter for zinc recovery. It was playing a significant role on the recovery of zinc and dissolution of iron. Increasing acid concentration caused increases in zinc recovery but also undesirable increases in iron dissolution.

Table 4.3: Effect of Acid Concentration on Zinc and Iron Recoveries in Acid Leaching

| Experimental Code | Acid Concentration (g/l) | Zn Recovery (%) | Fe Recovery (%) |
|-------------------|--------------------------|-----------------|-----------------|
| AL-0 | 0 | 18.4 | 7.1 |
| AL-1 | 50 | 56.2 | 11.6 |
| AL-2 | 100 | 66.8 | 32.0 |
| AL-3 | 150 | 70.8 | 47.4 |
| AL-4 | 250 | 72.6 | 52.3 |
| AL-5 | 350 | 73.5 | 60.0 |

Reaction Duration: 1 h, Reaction Temperature: 95°C, Solid/Liquid Ratio: 1/5 g/cc

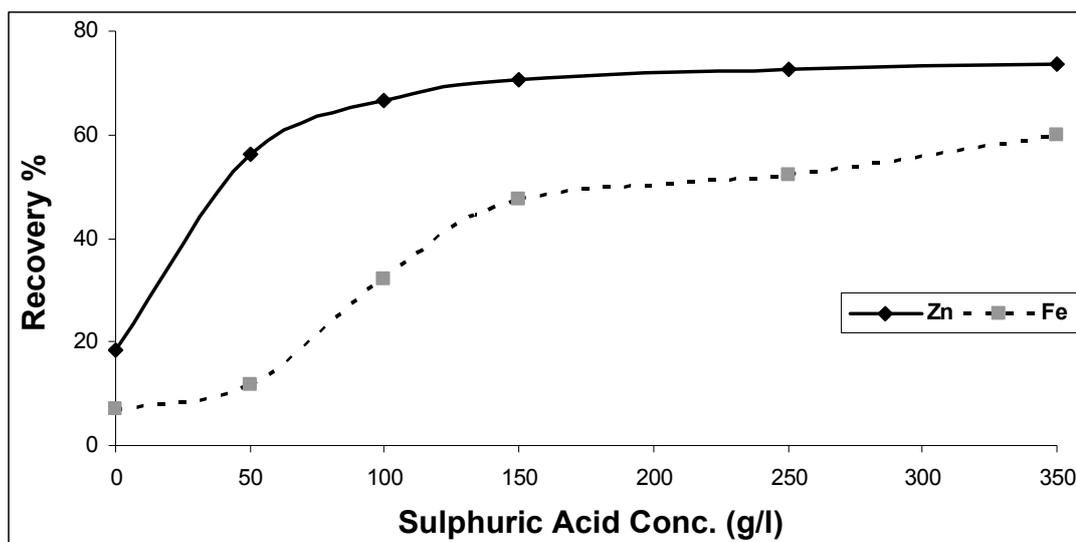


Figure 4.3: Effect of Acid Concentration on Zinc and Iron Recoveries in Acid Leaching

From the results, it can be concluded that sulphuric acid concentration should be higher than 100 g/l to obtain a substantial zinc recovery, but at the same time it

should be lower than 150 g/l to limit iron dissolution. It should also be kept in mind that the spent liquor generated as a result of zinc electrolysis which is to be used in acid leaching contains 150 g/l sulphuric acid. Moreover, other researchers who have studied leaching of zinc ferrite with sulphuric acid solution stated that sufficient zinc recoveries could be obtained by using more than 100 g/l H₂SO₄ at 90-95°C temperature range in 2-4 hours reaction duration [34, 37, 58].

4.3.2. Effect of Reaction Duration on Zinc Recovery in Acid Leaching

In order to see the effect of reaction duration on zinc recovery, leaching tests were carried out for 1, 2, 3, 6, 16, 24 and 32 hours. During these tests, other parameters such as; acid concentration, solid/liquid ratio, and reaction temperature were kept constant as 150 g/l, 1/5 g/cc, 95°C, respectively. The results of the experiments are given in Table 4.4 and Figure 4.4.

Table 4.4: Effect of Reaction Duration on Zinc and Iron Recoveries in Acid Leaching

| Experimental Code | Reaction Duration (h) | Zn Recovery (%) | Fe Recovery (%) |
|---|-----------------------|-----------------|-----------------|
| AL-3 | 1 | 70.8 | 47.4 |
| AL-6 | 2 | 71.9 | 49.0 |
| AL-7 | 3 | 73.4 | 50.9 |
| AL-8 | 6 | 74.9 | 57.9 |
| AL-9 | 16 | 80.0 | 64.5 |
| AL-10 | 24 | 82.8 | 70.9 |
| AL-11 | 32 | 82.8 | 72.1 |
| Acid Conc.:150 g/l, Reaction Temp.: 95°C, Solid/Liquid Ratio:1/5 g/cc | | | |

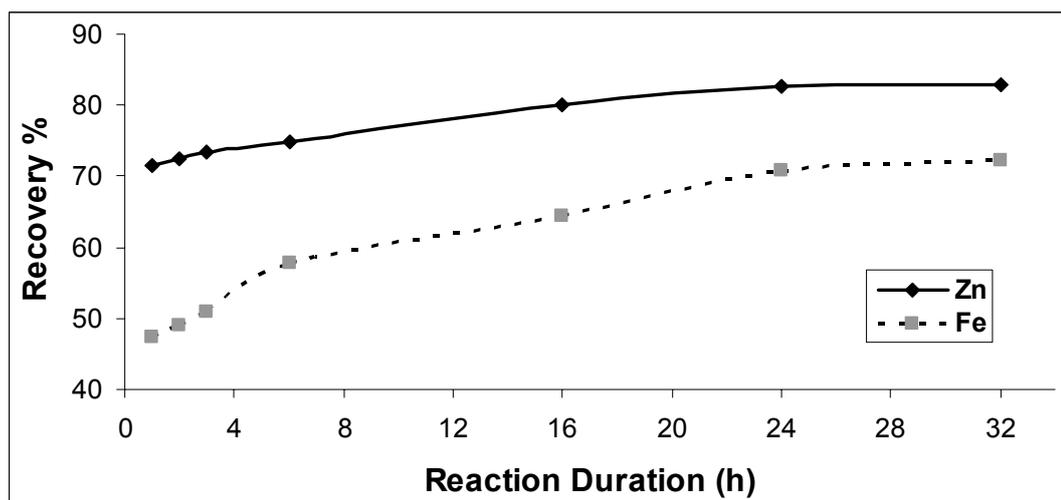


Figure 4.4: Effect of Reaction Duration on Zinc and Iron Recoveries in Acid Leaching

According to the results of experiments, it can be seen that increases in the reaction duration up to 24 hours caused increases in zinc recovery. There was no improvement in zinc recovery after 24 hours. The maximum value for zinc extraction of about 82.8% could be obtained at a temperature of 95°C, in a period of 24 hours and with a solid to liquid ratio 1/5 g/cc at a concentration of sulphuric acid of 150 g/l. On the other hand, the dissolution of iron was substantial as the leaching duration increased. This factor should be considered in deciding of the optimum reaction duration. In the following experiments, the duration of leaching was limited to 2 hours.

4.3.3. Effect of Reaction Temperature on Zinc Recovery in Acid Leaching

Since the reaction temperature during sulphuric acid leaching under atmospheric pressure has an important effect on zinc recovery, in this study the effect of leaching temperature was also investigated. For this purpose 30, 50, 75, and 95°C leaching temperatures were tested. During the tests, the following parameters were kept constant: Acid concentration: 150 g/l; solid-liquid ratio: 1/5 g/cc; reaction duration: 2 hours. Changes in zinc recoveries and iron dissolutions with increasing leaching temperature are given in Table 4.5 and Figure 4.5.

Table 4.5: Effect of Reaction Temperature on Zinc and Iron Recoveries in Acid Leaching

| Experimental Code | Reaction Temperature (°C) | Zn Recovery (%) | Fe Recovery (%) |
|-------------------|---------------------------|-----------------|-----------------|
| AL-12 | 30 | 63.7 | 22.3 |
| AL-13 | 50 | 65.6 | 33.8 |
| AL-14 | 75 | 67.3 | 40.0 |
| AL-6 | 95 | 71.9 | 49.0 |

Acid Conc.:150 g/l, Reaction Duration: 2 h, Solid/Liquid Ratio:1/5 g/cc

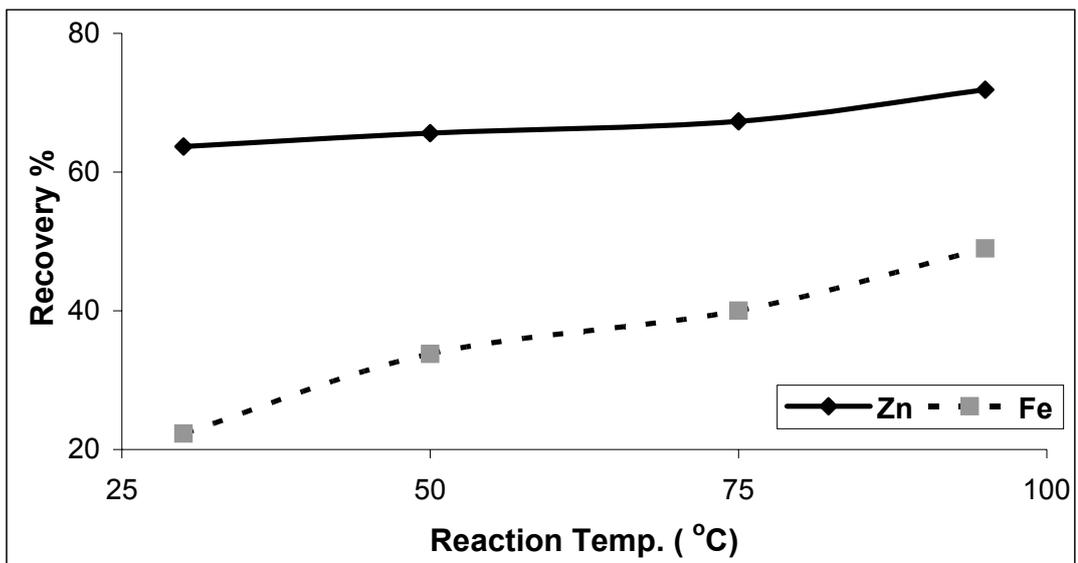


Figure 4.5: Effect of Reaction Temperature on Zinc and Iron Recoveries in Acid Leaching

These results indicated that increasing temperatures caused increasing zinc recoveries as well as iron dissolutions. Therefore, the optimum leaching temperature was chosen to be 95°C.

At this temperature, the leach solution containing 150 g/l H₂SO₄ does not boil. During boiling of the leach solution, it may not be necessary to stir the liquid. Therefore, at the end of the study on the effect of reaction temperature, the boiling point of leach solution having 150 g/l H₂SO₄ was determined as 99°C. After a trial at the boiling point without magnetic stirring, approximately 70.4% recovery of Zn was obtained with 150 g/l acid concentration in 2 hours reaction duration at 200 g/l pulp density. Under these conditions, the dissolution of iron was calculated as 42.2%. It can therefore be stated that stirring of the solution had a small positive effect on the recovery of zinc, but it negatively affected the iron dissolution.

4.3.4. Effect of Solid/Liquid Ratio on Zinc Recovery in Acid Leaching

In the study, in order to see the effect of pulp density three different solid-liquid ratios, namely 1/4, 1/5, and 1/6 g/cc, were investigated. During these experiments the other parameters were kept constant: Acid concentration: 150 g/l, reaction duration: 2 hours; reaction temperature: 95°C. The experimental results are given in Table 4.6 and in Figure 4.6.

Table 4.6: Effect of Solid/Liquid Ratio on Zinc and Iron Recoveries in Acid Leaching

| Experimental Code | Solid/Liquid Ratio (g/cc) | Zn Recovery (%) | Fe Recovery (%) |
|--|---------------------------|-----------------|-----------------|
| AL-15 | ¼ | 69.6 | 48.0 |
| AL-6 | 1/5 | 71.9 | 49.0 |
| AL-16 | 1/6 | 72.5 | 46.9 |
| Acid Conc.:150 g/l, Reaction Temp.: 95°C, Reaction Duration: 2 h | | | |

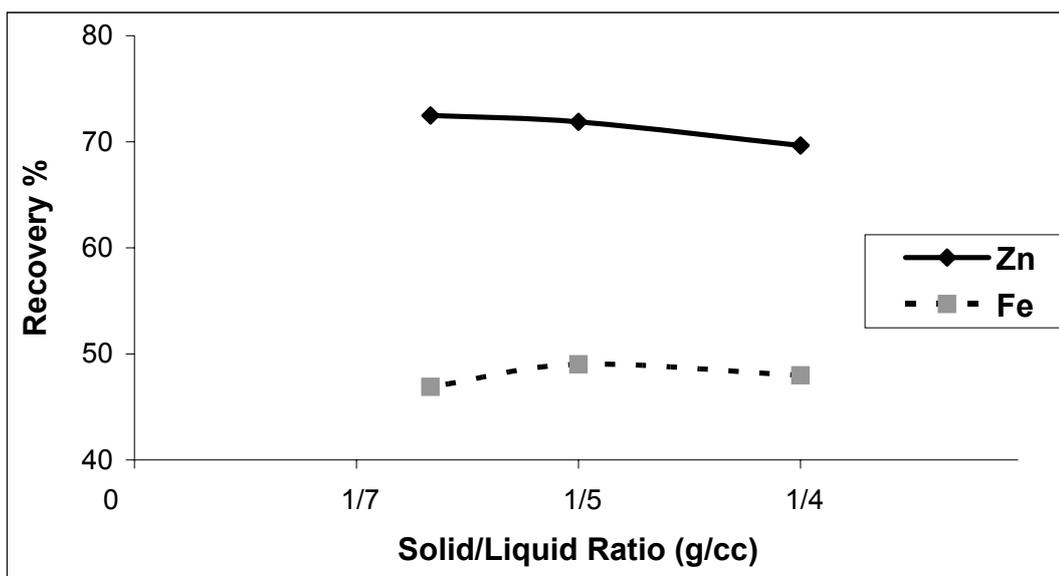


Figure 4.6: Effect of Solid/Liquid Ratio on Zinc and Iron Recoveries in Acid Leaching

From Figure 4.6, it is seen that the recovery of zinc slightly increased with decreasing pulp density. So, the change of solid/liquid ratio was very slightly effective on zinc recovery in the studied range.

In conclusion of sulphuric acid leaching experiments, it can be said that as zinc recovery increased, also iron dissolution increased. In order to minimize iron removal expenses at purification stage, acid concentration and reaction duration have to be limited. Therefore, the optimum hot acid leaching conditions were determined for the initial sulphuric acid concentration as 150g/l, reaction duration as 2 h, leaching temperature as 95°C, solid/liquid ratio as 1/5. At these conditions zinc recovery was found to be 71.9%. At longer leaching durations, the recovery of zinc could be increased but this would be accompanied by a substantial increase in iron contamination of the pregnant leach solution.

At the end of acid leaching of blended LR, in order to see the effect of the optimum hot acid leaching conditions on Turkish LR and Iranian LR, they were leached separately. Results of these experiments are given in Table 4.7.

Table 4.7: Acid Leaching of Turkish and Iranian Leach Residues

| Sample | Zn Recovery (%) | Fe Recovery (%) |
|---|-----------------|-----------------|
| Turkish LR | 68.8 | 46.5 |
| Iranian LR | 95.1 | 75.2 |
| Acid Conc.: 150 g/l, Reaction Temp.: 95°C, Reaction Duration: 2 h, Solid/Liquid Ratio: 1/5 (g/cc) | | |

As stated earlier, in acid leaching process, amount of zinc ferrite ($ZnFe_2O_4$) and zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$) in the LR determine the zinc recovery value. Therefore, in view of the Table 4.7, it can be said that the amounts of zinc ferrite ($ZnFe_2O_4$) and zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$) in Iranian LR were higher than those in Turkish LR.

It is seen from Table 4.7 that zinc recovery for Iranian LR was very high. But Iranian LR is limited in amount when compared to Turkish LR and in some places they are mixed with each other in Çinkur stockpile. Therefore, it can be said that the use of only Iranian LR is not very meaningful for zinc recovery. As a result, blended LR was used in all the remaining experiments.

Then, sufficient amount of blended LR was leached with sulphuric acid under the optimum hot acid leaching conditions in order to prepare a stock and to use in lead recovery experiments. After several experiments, approximately 1 kg of stock was prepared to be used in brine leaching part for lead recovery. In the stock preparation experiments, the average value of zinc recovery was calculated as 71.0%. Reproducible results were obtained in the range of $\pm 2\%$ of the stated value.

In order to determine the acidity of pregnant leach solution obtained after the chosen hot acid leaching trial (AL-6), titration of the pregnant leach solution was done by using 0.2 N NaOH. It is found that about 85 g/l of the initial 150g/l H_2SO_4 had remained in the solution after acid leaching. This result indicated that 65 g/l

H₂SO₄ was consumed for the recovery of zinc from zinc ferrite. Calculations done for this trial is given in Appendix A.

Considering the blended LR, it can be seen that acid consumption was almost completely spent by zinc ferrite. Therefore, the stoichiometrically needed acid consumption value was calculated in accordance with the zinc ferrite amount. Results of these calculations are given in Appendix B and C, showing that quantity of sulphuric acid used in the acid experiments was approximately twice as much as the stoichiometrically needed acid value.

At the end of water leaching experiments, the percentage of zinc originating from zinc heptahydrate was determined as 2.23%. In the same way, percentage of zinc originating from zinc ferrite was calculated by using the value obtained in Appendix B, ($12.43 \times 65 / 100 = 8.08\%$) which corresponded to 29.96% ZnFe₂O₄ ($8.08 \times 241 / 65 = 29.96\%$) in blended LR.

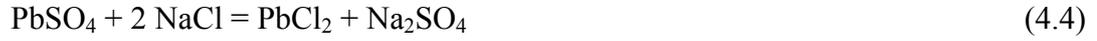
As mentioned in Chapter 2, iron removal process is needed before the zinc electrowinning step since pregnant solution obtained at the end of the optimum hot acid leaching includes high amount of iron. In order to remove from the solution, iron is precipitated as Hematite, Jarosite or Goethite which are the three types of commonly used iron removal processes. Although hematite product is more marketable, Jarosite process is more appropriate candidate due to more easily applicable method than others [35].

After removal of the iron in the solution by using one of the mentioned methods, pregnant leach solution goes through other purification stages to clean other impurities. Finally, electrolytic zinc can be obtained by electrowinning process [38].

4.4. Brine (NaCl) Leaching

After the hot sulphuric acid leaching experiments reasonably high zinc recoveries were accomplished with accompanied iron dissolution. In order to recover the lead present in the secondary leach residue, salt leaching experiments were decided to be performed. For this purpose, brine leaching experiments were done with 1 kg of

secondary leach residue obtained after H₂SO₄ leaching under the optimum conditions specified above. In order to recover lead from this residue, lead sulphate (PbSO₄), which is the only compound for recovery of lead in the secondary leach residue, is reacted with sodium chloride according to reaction (4.4) [45].



In brine leaching, NaCl concentration, S/L ratio (pulp density), reaction temperature, reaction duration, and HCl addition were chosen as variables. In the experiments, the recovery of lead was calculated according to the following equation (4.5):

$$\% \mathcal{R}_{Pb} = \left(\frac{W_{SLR} * C_{SLR} - W_{FLR} * C_{FLR}}{W_{SLR} * C_{SLR}} \right) * 100 \quad (4.5)$$

W_{SLR}: Weight of secondary leach residue in grams, W_{FLR}: Weight of final leach residue in grams, C_{SLR}: Weight percent (Concentration) of metal (Pb) in secondary leach residue, C_{FLR}: Weight percent (Concentration) of metal (Pb) in final leach residue.

4.4.1. Effect of NaCl Concentration on Lead Recovery in Brine Leaching

For investigation of NaCl concentration on lead recovery, six different concentrations from 50 g/l to 350 g/l were tested at the following constant conditions; Solid/liquid ratio: 1/20 g/cc; reaction duration: 15 minutes; reaction temperature: 25°C. The experimental results are given in Table 4.8 and plotted in Figure 4.7.

Table 4.8: Effect of NaCl Concentration on Lead Recovery in Brine Leaching

| Experimental Code | NaCl Concentration (g/l) | Pb Recovery (%) |
|-------------------|--------------------------|-----------------|
| BL-1 | 50 | 4.0 |
| BL-2 | 100 | 7.9 |
| BL-3 | 150 | 32.9 |
| BL-4 | 200 | 62.7 |
| BL-5 | 250 | 82.0 |
| BL-6 | 300 | 95.0 |

Reaction Duration:15 min., Reaction Temp.:25°C, Solid/Liquid Ratio: 1/20 g/cc

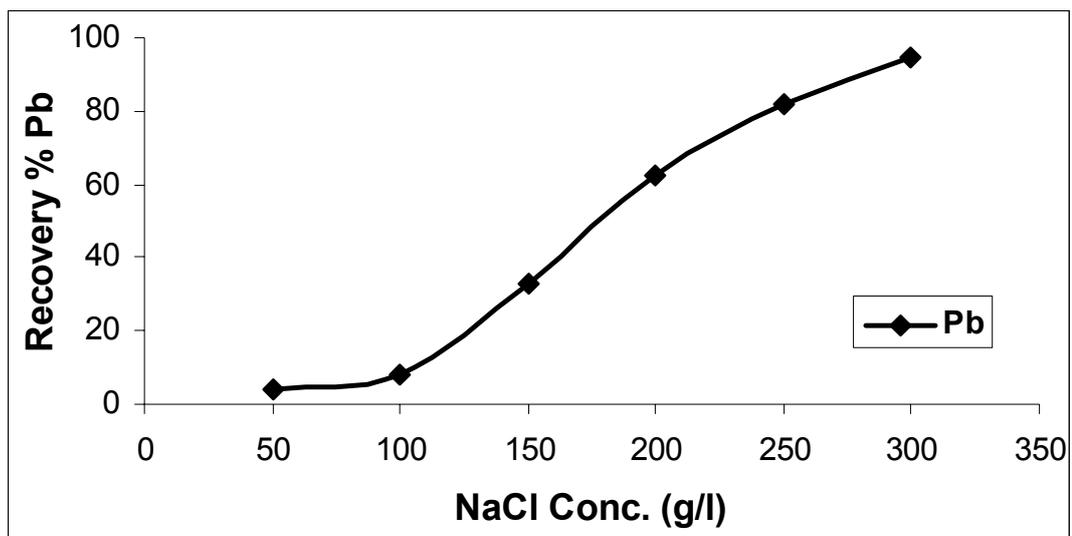


Figure 4.7: Effect of NaCl Concentration on Lead Recovery in Brine Leaching

From these results, it can be concluded that the brine concentration is a very effective parameter for lead recovery. As the NaCl concentration increased, lead recovery increased significantly. Therefore, NaCl concentration should be chosen as high as possible. However, it is suggested not to use greater than 350 g/l NaCl

concentration in brine leaching because when greater values are used NaCl solution becomes saturated. NaCl solubility in grams per 100 cc cold water is given as 35.7 [1]. This means that maximum NaCl concentration can be chosen as 357 g/l.

Several researchers emphasized that in the solutions having high chloride concentration, $PbCl_2$ converts to $PbCl_3^-$ and then to $PbCl_4^{2-}$ complexes according to reactions (4.6 and 4.7) due to their solubilities being higher than $PbCl_2$. This results in a increase in the concentration of Pb^{2+} ions in solution [9, 32, 59].



4.4.2. Effect of Solid/Liquid Ratio on Lead Recovery in Brine Leaching

For this study, in order to see the effect of pulp density, the solid to liquid ratio was varied between 1/5 and 1/40 g/cc when NaCl concentration, reaction temperature and duration were kept as 250 g/l, 25°C and 15 minutes, respectively. The experimental results are summarized in Table 4.9 and plotted in Figure 4.8. As seen from Figure 4.8 that the lead recovery decreases with increasing pulp density.

Table 4.9: Effect of Solid/Liquid Ratio on Lead Recovery in Brine Leaching

| Experimental Code | Solid/Liquid Ratio (g/cc) | Pb Recovery (%) |
|--|---------------------------|-----------------|
| BL-8 | 1/5 | 20.3 |
| BL-9 | 1/10 | 45.2 |
| BL-5 | 1/20 | 82.0 |
| BL-10 | 1/30 | 94.6 |
| BL-11 | 1/40 | 96.3 |
| NaCl Conc.: 250 g/l, Reaction Duration: 15 min., Reaction Temp.:25°C | | |

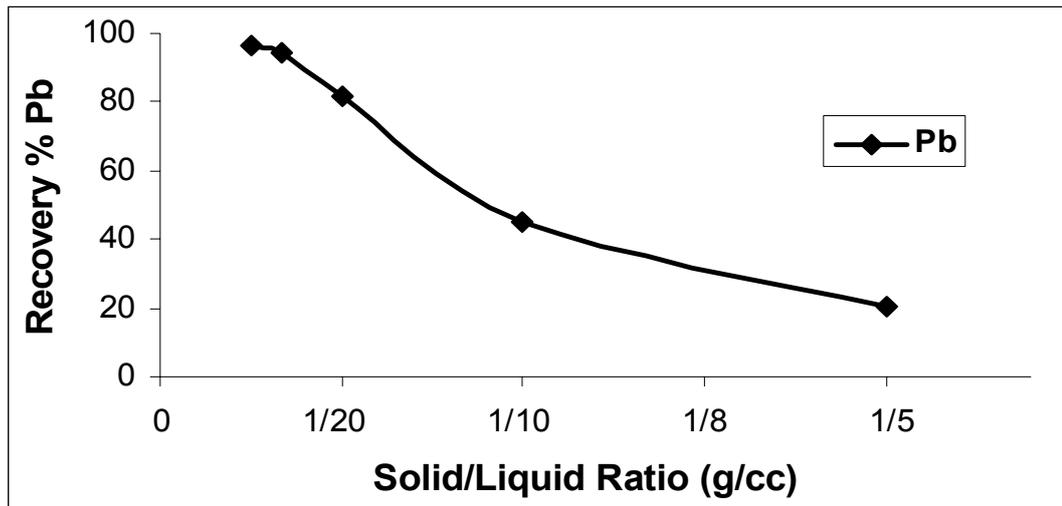


Figure 4.8: Effect of Solid/Liquid Ratio on Lead Recovery in Brine Leaching

It was seen from the results that the highest lead recovery was obtained with 1/40 solid to liquid ratio. However, this pulp density is unreasonably low for economical use. When higher pulp densities were used, decreases in lead recoveries were observed. The reason of this decrease was thought to be due to the fact that NaCl concentration around residue particles was insufficient for dissolution of lead in liquid NaCl solution.

4.4.3. Effect of HCl addition on Lead Recovery in Brine Leaching

Many researchers stated that lead solubility significantly increases with increasing chloride ion, Cl^- , in the solution [45, 46, 60, 61]. They added HCl to the leaching solution with the aim of increasing the activity of Cl^- ions and to obtain maximum lead recovery. For this purpose, in this study, 10 ml/l HCl was added to various leach solutions at the following constant conditions: NaCl concentration: 300 g/l; reaction duration: 30 minutes; reaction temperature: 25°C. Results of these trials are tabulated in Table 4.10 and presented in Figure 4.9. Results indicated that HCl addition had slightly affected lead recovery.

Table 4.10: Effect of HCl Addition on Lead Recovery at Various Solid/Liquid Ratios in Brine Leaching

| Experimental Code | Solid/Liquid Ratio (g/cc) | Pb Recovery (%) | HCl Addition (ml/l) |
|-------------------|---------------------------|-----------------|---------------------|
| BL-12 | 1/4 | 24.2 | 0 ml |
| BL-13 | 1/5 | 31.6 | 0 ml |
| BL-14 | 1/10 | 69.6 | 0 ml |
| BL-15 | 1/20 | 94.5 | 0 ml |
| BL-16 | 1/4 | 27.8 | 10 ml |
| BL-17 | 1/5 | 35.3 | 10 ml |
| BL-18 | 1/10 | 77.8 | 10 ml |
| BL-19 | 1/20 | 98.3 | 10 ml |

NaCl Conc.: 300 g/l, Reaction Duration: 30 min., Reaction Temp.:25°C

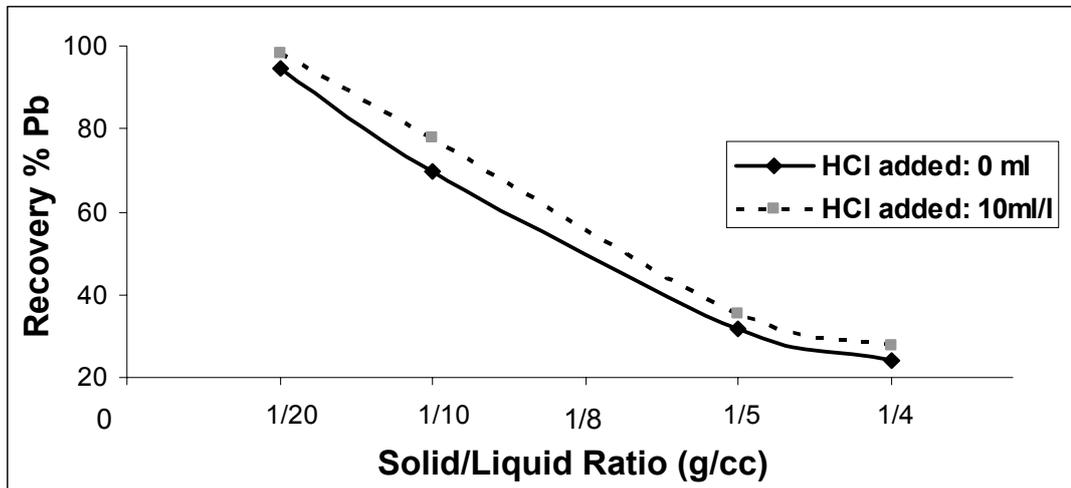


Figure 4.9: Effect of HCl Addition on Lead Recovery at Various Solid/Liquid Ratios in Brine Leaching

4.4.4. Effect of Reaction Temperature on Lead Recovery in Brine Leaching

It is known that reaction temperature is one of the most important factors which affect the brine leaching process. In this study, the effect of temperature was investigated for the leaching temperatures of 25, 50, 80, 95°C as well as at the boiling point of 102°C. During the tests, NaCl concentration (300 g/l), reaction duration (60 minutes) and solid to liquid ratio (1/5 g/cc) were kept constant. The results of the experiments are given in Table 4.11 and presented in Figure 4.10.

Table 4.11: Effect of Reaction Temperature on Lead Recovery in Brine Leaching

| Experimental Code | Reaction Temp. (°C) | Pb Recovery (%) |
|-------------------|---------------------|-----------------|
| BL-20 | 25 | 33.2 |
| BL-21 | 50 | 40.3 |
| BL-22 | 80 | 72.9 |
| BL-23 | 95 | 78.8 |
| BL-24 | 102 | 79.8 |

NaCl Conc.: 300 g/L, Reaction Duration: 60 min., Solid/Liquid Ratio:1/5 g/cc

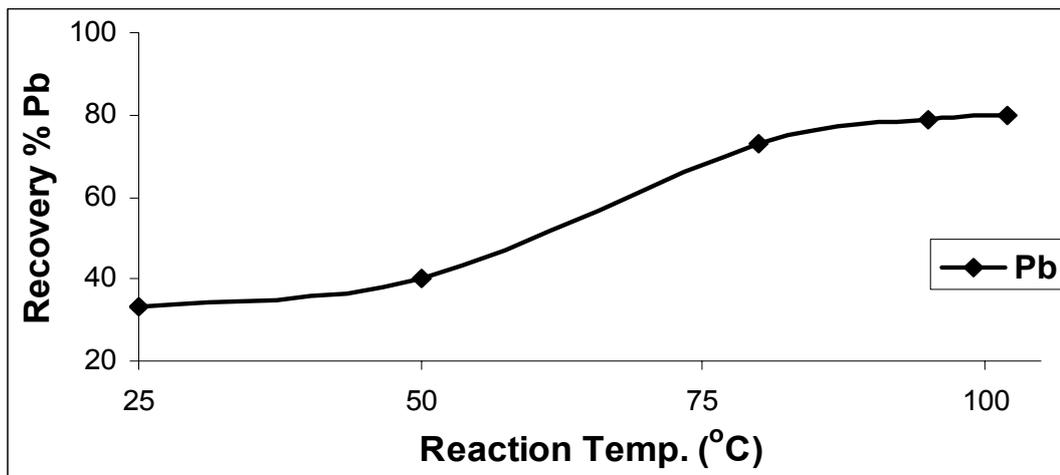


Figure 4.10: Effect of Reaction Temperature on Lead Recovery in Brine Leaching

As seen from the results, the brine leaching temperature was a very effective parameter for lead recovery. Increases in the temperature beyond 50°C caused a substantial increase in lead recovery. This implies that the brine leaching temperature should be greater than 50°C. In addition, according to Habashi [62], while solubility of PbSO₄ in 0.25 N NaCl is 0.35 g/l at 25°C, it reaches 6.90 g/l at 120°C. It is shown that as the temperature increases, the solubility of lead also increases.

4.4.5. Effect of Reaction Duration on Lead Recovery in Brine Leaching

The effect of reaction duration on brine leaching was investigated by varying the reaction duration between 5 to 300 minutes. During the tests the following parameters were kept constant: NaCl concentration: 300 g/l; reaction temperature 95°C; solid/liquid ratio: 1/5 g/cc. The results of the experiments are seen in Table 4.12 and Figure 4.11.

Table 4.12: Effect of Reaction Duration on Lead Recovery in Brine Leaching

| Experimental Code | Reaction Duration (min.) | Pb Recovery (%) |
|---|--------------------------|-----------------|
| BL-25 | 5 | 82.4 |
| BL-26 | 10 | 84.9 |
| BL-27 | 15 | 82.8 |
| BL-28 | 30 | 79.7 |
| BL-23 | 60 | 78.8 |
| BL-29 | 180 | 74.6 |
| BL-30 | 300 | 73.1 |
| NaCl Conc.: 300 g/l, Reaction Temp.: 95°C , Solid/Liquid Ratio:1/5 g/cc | | |

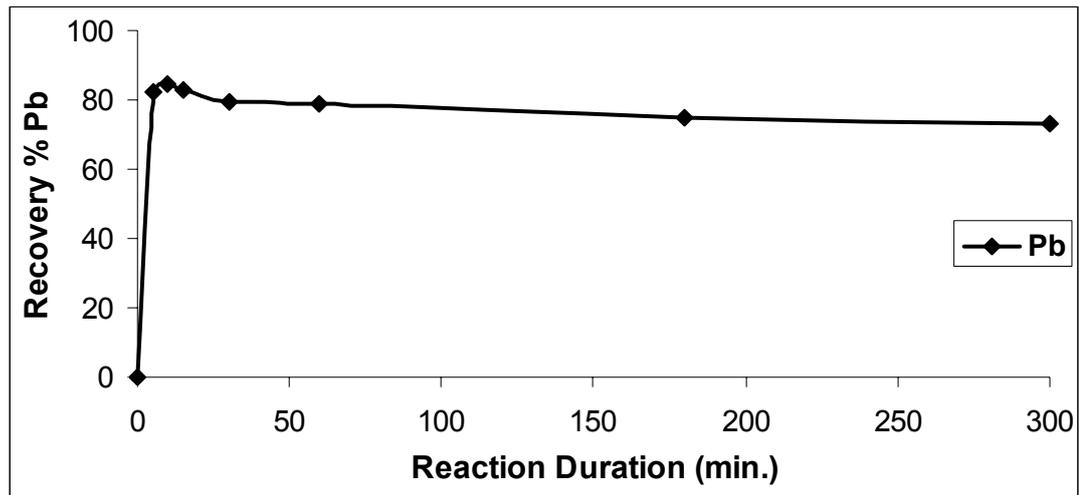


Figure 4.11: Effect of Reaction Duration on Lead Recovery in Brine Leaching

From Figure 4.11 it can be seen that the increases in the reaction duration beyond 10 minutes caused a gradual decrease in lead recovery. This was most probably due to the precipitation of lead in solution i.e., reversion of reaction. A similar kind of decrease in lead recovery with increasing reaction duration was also observed by other researchers [61]. Therefore, the reaction duration should be controlled in between 5 to 15 minutes.

After the brine leaching experiments, it is shown that the maximum lead recovery obtainable was 84.9% when the experimental parameters were chosen for NaCl concentration as 300 g/l, reaction temperature as 95°C, solid/liquid ratio as 1/5 g/cc and reaction duration as 10 minutes. Meanwhile in brine leaching, not only lead was recovered from the residue but also zinc and iron were dissolved in the solution about 8% and 5%, respectively.

Lastly, in order to see the effect of HCl addition to the experiment performed at the optimum conditions 10 ml/l HCl added to the brine leaching solution. As seen in Table 4.13, after HCl addition lead recovery increased from 84.9 % to 89.0 %. However, the cost of HCl should be taken into consideration before recommending the use of HCl.

Table 4.13: Effect of HCl Addition at the Optimum Brine Leaching Conditions

| Experimental Code | Solid/Liquid Ratio (g/cc) | Pb Recovery (%) | HCl Addition (ml/l) |
|---|---------------------------|-----------------|---------------------|
| BL-26 | 1/5 | 84.9 | 0 ml |
| BL-31 | 1/5 | 89.0 | 10 ml |
| NaCl Conc.: 300 g/l, Reaction Duration: 10 min, Reaction Temp.:95°C | | | |

In addition, in view of the lead content in the secondary leach residue, a stoichiometric calculation was performed for the optimum brine leaching conditions. According to this calculation given in the Appendix D, the amount of NaCl used in brine leaching is equal to almost 13 times of the stoichiometrically needed amount for the secondary leach residue.

At the end of brine leaching, lead must be recovered from the pregnant salt solution. Final leach liquor contains Pb^{2+} ions, together with low concentrations of dissolved Zn, Fe and others. In order to separate dissolved lead from other metals, several methods can be used such as cementation, electrowinning, ion exchange or crystallization of $PbCl_2$ by cooling the pregnant leaching solution [60]. Any appropriate method can be applied to obtain lead from the solution after purification stage.

4.5. Final Comments on the Results

As mentioned previously, in this study, BLR was the starting material. After H_2SO_4 leaching of BLR to improve zinc recovery, secondary leach residue (SLR) was obtained. NaCl leaching of SLR for lead recovery generated a residue called final leach residue (FLR). Chemical analyses of these residues are given in Table 4.14.

Table 4.14: Chemical Analyses of Blended, Secondary and Final Leach Residues

| Component | Blended LR (wt %) | Secondary LR (wt %) | Final LR (wt %) |
|--------------------------------|----------------------|------------------------|--------------------|
| Pb | 15.51 | 20.51 | 4.57 |
| Zn | 12.43 | 4.71 | 5.81 |
| Fe | 6.27 | 4.18 | 6.62 |
| Cd | 0.05 | 0.016 | 0.023 |
| SO ₃ | 20.48 | 22.34 | 18.84 |
| SiO ₂ | 17.35 | 25.03 | 38.47 |
| CaO | 7.57 | 7.99 | 9.90 |
| Al ₂ O ₃ | 3.99 | 3.79 | 5.48 |
| MnO | 0.79 | 0.17 | 0.18 |
| MgO | 0.98 | 0.39 | 0.41 |
| K ₂ O | 0.14 | 0.22 | 0.47 |
| BaO | 0.36 | 0.49 | 0.65 |

As it can be seen from Table 4.14, Pb content is originally 15.51% in the BLR. After acid leaching, secondary LR is obtained and the amount of Pb increases from 15.51% to 20.51% in the solid part due to the fact that PbSO₄ is not leached in sulphuric acid and the amount of solid residue decreases in weight by about 30%. Similarly, after brine leaching, the weight of secondary LR declines further by approximately 30% and final LR is obtained. In other words, more than half of the blended leach residue is lost in weight until obtaining the final leach residue. It is seen from Table 4.14 that these weight changes affect percents of the all dissolved and undissolved elements in the residues. For example, while iron percent is 6.27% in blended LR, it decreases to 4.18% then increases to 6.62% after acid and brine leaching, respectively. That is, compounds including iron dissolve in acid leaching

and so the value of iron percentage decreases to 4.18% after acid leaching but it increases to 6.62% after brine leaching due to little amount iron dissolution. Both silicates and complex compounds are other examples. Since they are not dissolved in both leachants (acid and brine); SiO₂, CaO, BaO, Al₂O₃ percents in the residues tend to increase.

According to the results of analyses, it was shown that the final LR contained approximately 5.8% zinc. Zinc in the final LR was mostly in the form of silicate and complex oxides, which are not soluble in H₂SO₄ and NaCl solutions [1]. However, final LR also contains small value of undissolved zinc ferrite since all of the ZnFe₂O₄ was not dissolved at the optimum hot acid leaching condition. Considering this point and total weight losses in the residue after two leaching steps, it can be said that the total percentage of zinc originating from zinc silicate and zinc complex forms in the blended LR was about 2.11%. This value indicated that total zinc in zinc silicate and complex compounds was roughly 17%. As explained earlier, blended LR contained different zinc compounds as zinc sulphate, zinc ferrite, zinc silicate and complex zinc oxides. In the light of this knowledge, the percentage of all zinc forms determined as well as their zinc contributions can be seen in Table 4.15.

Table 4.15: Determination of Zinc Compounds in Blended LR

| Zinc Forms | Percentage of Zn Originating from Different Zinc Compounds | Percentage of Zinc Compounds in BLR |
|----------------------|--|-------------------------------------|
| Sulphate | $12.43 \times 18 / 100 = 2.23$ | 9.85 |
| Ferrite | $12.43 \times 65 / 100 = 8.08$ | 29.96 |
| Silicate and Complex | $12.43 \times 17 / 100 = 2.11$ | 3.60* |
| TOTAL | 12.43 | 43.41 |

* Neglecting complex zinc oxides and assuming complete dissolution of zinc ferrite in acid leaching.

After the determination of zinc compound percents in blended LR, it was also necessary to calculate the percentage of lead sulphate. BLR contains 15.51% Pb and all of lead is present as lead sulphate (PbSO_4) so lead sulphate percent ($15.51 \times 303 / 207 = 22.70$) was found to be 22.70% in the blended LR. Sum of the zinc and lead compounds percentage in the BLR was calculated as 66.11%. It was considered that the remaining part of BLR is composed of some compounds including mainly Ca, Fe, Si and Al.

With respect to lead, as noted before lead sulphate does not dissolve in sulphuric acid. Therefore, only brine leaching part is related to the lead recovery. From Table 4.14, it is seen that lead content decreased from %20.51 to about 4.6% after NaCl leaching. In the view of weight loss, this means that more than 80% Pb recovery was achieved at the end of brine leaching.

The XRD patterns of BLR, SLR and FLR are given in Figure 4.12. As seen from the patterns, almost all of the $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (zinc sulfate heptahydrate) and ZnFe_2O_4 (zinc ferrite) were leached at the end of acid leaching. On the other hand, it is seen from the XRD pattern of the final LR that, most of the PbSO_4 (lead sulphate) was leached from the SLR after the brine leaching. In other words, the peaks of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and ZnFe_2O_4 were almost completely removed in the acid leaching process and after brine leaching process PbSO_4 peaks were lowered. Moreover, minor phases such as zinc silicate, iron silicate and others were still observed in the XRD pattern of the final LR. This was the result of their low solubilities in sulphuric acid and brine.

All these results are also supported by SEM analyses of the final LR obtained after the optimum NaCl leaching as given in Figure 4.13 and Table 4.16. As seen from the Figure 4.13, Pb and Zn peaks had lowered compared to their peaks of the SEM analyses result of blended LR given in Figure 3.6. On the other hand, other compounds containing Al and Na were determined in the SEM figure of the final LR while they are not detected in the XRD pattern of the final LR. This is due to the fact that they are found in small amount in the final LR.

Full scale counts: 814

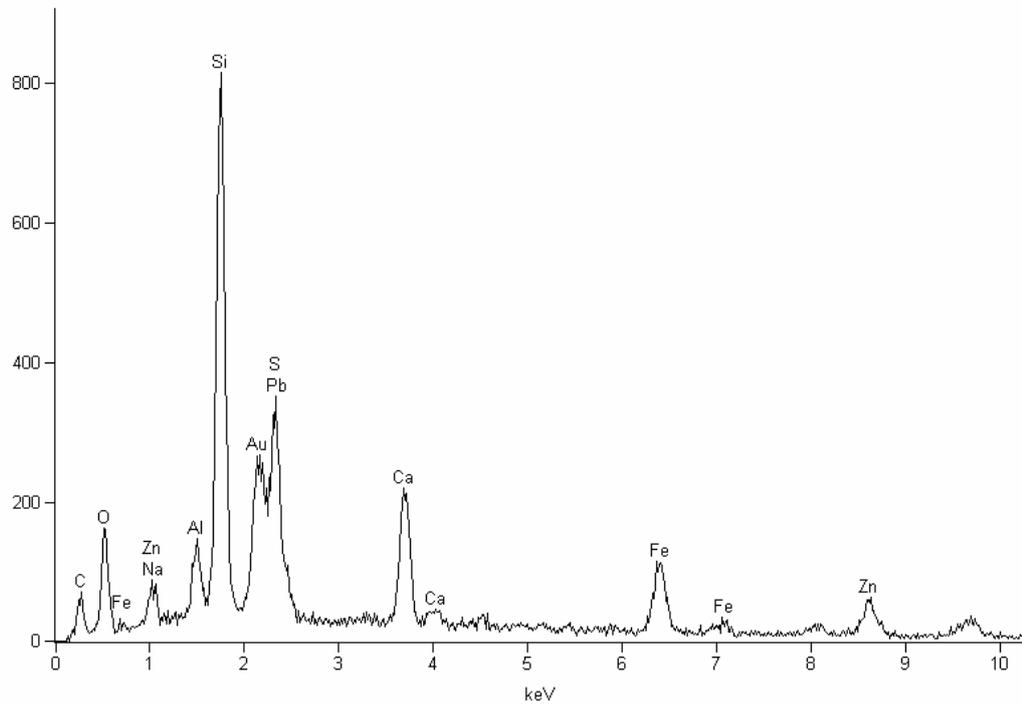


Figure 4.13: SEM Analyses of Final Leach Residue

Table 4.16: EDS Analysis of Final Leach Residue

| Element | Weight Concentration (%) | Atom Concentration (%) |
|---------|--------------------------|------------------------|
| Pb | 5.01 | 0.57 |
| Zn | 7.52 | 2.71 |
| Fe | 5.98 | 2.52 |
| O | 43.97 | 64.74 |
| Si | 20.33 | 17.05 |
| S | 7.38 | 5.42 |
| Ca | 6.25 | 3.67 |
| Al | 2.26 | 1.98 |
| Na | 1.30 | 1.33 |

CHAPTER V

CONCLUSIONS

In this study, it was aimed to recover zinc and lead from Çinkur leach residue together with dissolution of iron under various conditions by using aqueous solutions, namely water, sulphuric acid and brine. For this purpose, blended leach residue (BLR) was prepared by mixing of 9 parts Turkish LR and 1 part Iranian LR in relation to their amounts in the Çinkur stockyard. Before that, the physical, chemical and mineralogical characterization of these leach residues were performed. After characterization, it was seen that zinc and lead content in the BLR are 12.43% and 15.51%, respectively. In addition, the XRD examination of BLR revealed that PbSO_4 and $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ were the major, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, ZnFe_2O_4 , Zn_2SiO_4 , Fe_2O_3 , SiO_2 and CaSiO_4 were minor components in the investigated sample.

Initial leaching experiments were done with water to see the effect of dissolution of the residue in water. From the XRD results it was seen that water soluble compound, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, existed in the BLR so it was expected that certain amount of zinc could be recovered after water leaching. At the end of acid leaching trials, the maximum zinc recovery was determined to be approximately 18%.

Due to this insufficient zinc recovery of water leaching, acid leaching experiments were done for zinc recovery. Sulphuric acid (H_2SO_4) was decided to be used since ZnFe_2O_4 in the LR is soluble in the acid solution. In acid leaching, it was observed that zinc recovery increased with increasing acid concentration, reaction duration

and leaching temperature. Also, it increased slightly with decreasing solid/liquid ratio. Therefore, hot acid leaching conditions were chosen as 150 g/l initial sulphuric acid concentration, 2 h reaction duration, 95°C leaching temperature and 1/5 solid/liquid ratio with a zinc recovery of about 72%.

After obtaining a reasonable amount of zinc by leaching in H₂SO₄ solution, brine (NaCl) leaching experiments were done to recover lead. Brine leaching experiments were conducted with the secondary leach residue containing 20.51% Pb obtained after H₂SO₄ leaching. It was seen that NaCl concentration and solid/liquid ratio (pulp density) were very effective parameters on lead recovery at room temperature brine leaching. HCl addition in brine leachant caused minor effects on recovery of lead. Lead recoveries up to 98 % could be obtained at a very low pulp density (50 g/l) in laboratory scale after HCl addition to the NaCl solution.

In order to use this technique in industrial scale, high pulp density should be used. Moreover, for reasonable recovery of lead by using high pulp density, temperature of the leaching solution should be increased. For this purpose, several trials were carried out with high pulp density (200 g/l) at 95°C. During a study on the effect of reaction duration, it was seen that lead recovery did not increase after 10 minutes. This finding indicated that the leaching duration should be controlled in between 5 to 15 minutes. As a result, the optimum brine leaching conditions were determined as 300 g/l NaCl concentration, 200 g/l pulp density, 10 min reaction duration and 95 °C leaching temperature with about 85% lead recovery. The chemical composition of final leach residue obtained after optimum brine leaching showed that it contained 4.57% Pb and 5.81% Zn as well as 6.62% Fe.

Although a reasonable amount zinc and lead were recovered from the blended Çinkur leach residue after acid and brine leaching steps, it is necessary to evaluate the economics of the suggested process before industrial application.

Future work recommended:

1. After brine leaching, cementation of lead from the pregnant solution should be studied. It can be performed with aluminum, zinc or iron.

2. After hot acid leaching for zinc recovery, secondary leach residue can be treated with sodium sulphide (Na_2S) solution to convert PbSO_4 into PbS . After floatation of PbS , lead can be obtained by pyrometallurgical treatment of PbS concentrate.
3. Initially the blended leach residue can be subjected to NaCl solution to produce PbCl_2 and then precipitation of lead sulphide (PbS) from the solution can be done by adding Na_2S . This approach can also be investigated to recover lead.
4. Pyrometallurgical methods like Ausmelt and Kivcet can also be investigated for the recovery of lead and zinc from leach residue.
5. Experiments can be conducted with various ammoniacal solutions i.e., NH_4Cl , NH_4OH , $(\text{NH}_4)_2\text{SO}_4$, or $\text{CH}_3\text{COONH}_4$ to recover lead from leach residue.

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APPENDIX A

CALCULATION OF FREE ACID BY TITRATION OF THE PREGNANT LEACH SOLUTION OBTAINED AFTER THE CHOSEN ACID LEACHING TRIAL

In order to determine acidity of leach solution obtained after the chosen acid leaching trial, the acid-base titration method was used. For this purpose, the pregnant leach solution was titrated with 0.2 N NaOH.

Preparation of Solutions:

In order to prepare titration solution with 0.2 N NaOH, 8 g NaOH was dissolved in the 1000 ml de-ionized water. (Molecular weight of NaOH = 40 g/mole)

In addition, the standard acid solution having 100 g/l H₂SO₄ was prepared to use in calculations.

Method:

Firstly, 5 ml standard solution was taken and completed to 25 ml with de-ionized water. Methyl red was also added as indicator and potassium oxalate was used to hold iron in the solution. Then, this solution was titrated with 0.2 N NaOH and it was determined that 100 g/l H₂SO₄ solution consumed 50.4 g NaOH.

Table A.1: Calculating of Titration of Pregnant Leach Solution

| | Consumed NaOH (ml) | Calculations | Amount of H ₂ SO ₄ (g/l) |
|--------------|-----------------------|--------------------------|---|
| First trial | 43.1 | $43.1 \times 100 / 50.4$ | 85.5 |
| Second trial | 42.9 | $42.9 \times 100 / 50.4$ | 85.1 |
| Third trial | 42.8 | $42.8 \times 100 / 50.4$ | 84.9 |
| Average | 42.9 | | 85.2 |

Free acid of pregnant leach liquor obtained after the chosen acid leaching conditions (experiment AL-6) was determined as approximately 85 g/l H₂SO₄.

APPENDIX B

DETERMINATION OF ZINC FORMS IN BLENDED LEACH RESIDUE

From XRD result (Figure 3.3) it can be deduced that three types zinc compounds namely zinc sulphate heptahydrate, zinc ferrite and zinc silicate exist in blended LR. It is known that zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) is soluble in the water, zinc ferrite (ZnFe_2O_4) is soluble in the concentrate sulphuric acid and zinc silicate (Zn_2SiO_4) is not soluble in either water or sulphuric acid.

Therefore, during acid leaching, among the zinc compounds only $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and ZnFe_2O_4 dissolve in the solution. In the acid leaching results, the maximum zinc recovery (~83%) was achieved in the experiment AL-11. If it can be assumed that all of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and ZnFe_2O_4 dissolved after experiment AL-11, then it can be inferred that 65% Zn recovery resulted from zinc ferrite compound because of 18% Zn recovery to be coming from water soluble $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Then, it can be said that after acid leaching, the remaining zinc was present as zinc silicate in the secondary LR. To sum up, it is found that 18% and 65% zinc recoveries arise from $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and ZnFe_2O_4 , respectively. These values are valid only for the maximum zinc recovery conditions: Acid concentration: 150 g/l, reaction temperature: 95°C, solid/liquid ratio: 1/5 g/cc and reaction duration: 32 h.

On the other hand, after optimum hot acid leaching trial zinc recovery value was obtained about 72%. This means that zinc recovery originated from zinc sulphate heptahydrate (18%) and zinc ferrite (54%). On the basis of this calculation, it can be said that the amount of soluble zinc ferrite in the zinc compounds is about 54%

under optimum acid leaching conditions. Therefore, calculating the stoichiometric ratio in Appendix C, it was assumed that 54% of total zinc compounds in the BLR are formed by zinc ferrite and reacted with H_2SO_4 .

APPENDIX C

CALCULATION OF THE STOICHIOMETRIC H₂SO₄ CONSUMPTION FOR THE LEACH RESIDUE

This calculation was done for the chosen hot acid leaching conditions; solid/liquid ratio (gram/cm³):1/5, acid concentration: 150 g/l, reaction duration: 2 h and reaction temperature: 95°C.

Weight of blended leach residue (used): 20 g. So, liquid = 5*20 = 100 cm³ (or ml)
Mass of elements and compounds (g/mole): Zn = 65.39, H₂SO₄ = 98.07.

Merck quality sulphuric acid 95-98 wt %; (95+98)/2 = 96.5 wt % (taken)

Weight of required acid = 15 g; 15*(100/96.5) = 15.5 g

15.5 g sulphuric acid with 95-98 wt % was added to get predefined 100 ml acidic solution.

Volume of the required acid = 15.5/1.84 = 8.4 ml H₂SO₄, (Density of H₂SO₄ = 1.84 g/cm³)

Volume of the required water = 100 – 8.4 = 91.6 ml H₂O, (Density of the H₂O = 1 g/cm³)

To sum up, 8.4 ml H₂SO₄ and 91.6 ml H₂O were used to prepare the 100 ml acidic solution.

Since zinc content in the blended leach residue is 12.43% and zinc ferrite in the zinc compounds is about 54%;

Weight of Zn in zinc ferrite = $20 \times (12.43/100) \times 0.54 = 1.342$ g,

Mole number of zinc ferrite = $1.342/65.39 = 0.0205$ moles.

According to reaction 4.2, stoichiometrically, 4 moles of sulphuric acid consumes 1 mole of zinc ferrite. Therefore;

Mole number of required acid = $0.0205 \times 4 = 0.082$ moles.

Mole number of used acid = $15.5/98.07 = 0.158$ moles.

Therefore, the stoichiometric ratio = $0.158/0.082 = 1.92$

APPENDIX D

CALCULATION OF THE STOICHIOMETRIC NaCl CONSUMPTION FOR THE SECONDARY LEACH RESIDUE

This calculation was done for the optimum brine leaching conditions; solid/liquid ratio (gram/cm³): 1/5, NaCl concentration: 300 g/l, reaction duration: 2 h and reaction temperature: 95°C.

Weight of secondary leach residue: 20 g. So, liquid = 5*20 = 100 cm³ (or ml)

Mass of elements and compounds (g/mole): Pb = 207.2, NaCl= 58.44,

Merck quality sodium chloride 99.5 wt %;

Weight of required NaCl = 30 g

30 g NaCl with 99.5 wt % purity was added to water to get 100 ml salt solution.

Lead content in the secondary LR is 20.51% and only lead sulphate is the source of lead in the residue. Therefore, all of the lead reacts with sodium chloride.

Weight of Pb in the secondary LR = 20*(20.51/100) = 4.102 g,

Mole number of lead sulphate = 4.102/207.2 = 0.0198 moles.

According to reaction 4.4, stoichiometrically, 2 moles of sodium chloride consumes 1 mole of lead sulphate. Therefore;

Mole number of required salt = 0.0198*2 = 0.0396 moles.

Mole number of used salt = (30*0.995)/58.44 = 0.5108 moles.

Therefore, the stoichiometric ratio = 0.5108/0.0396 = 12.90