# INVESTIGATION AND DEVELOPMENT OF POSSIBLE LEACHING PROCESSES FOR RECOVERY OF ZINC AND LEAD FROM ÇİNKUR LEACH RESIDUES

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AHMET SEMİH SUNKAR

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Approval of the Graduate School of Natural and Applied Science

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Tayfur Öztürk
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Yavuz A. Topkaya
Supervisor

Examining Committee Members

| | |
|---|---|
| Prof. Dr. Ahmet Geveci | (METU, METE) |
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Ahmet Semih, Sunkar

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# ABSTRACT

## INVESTIGATION AND DEVELOPMENT OF POSSIBLE LEACHING PROCESSES FOR RECOVERY OF ZINC AND LEAD FROM ÇİNKUR LEACH RESIDUES

Sunkar, Ahmet Semih

M.S., Department of Metallurgical and Materials Engineering
Supervisor: Prof. Dr. Yavuz A. Topkaya
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The major aim of this study was to investigate various leaching methods for the recovery of zinc and lead from blended neutral leach residues of Çinkur having a composition of 12.59 % Zn, 15.21 % Pb, 6.45 % Fe, 0.054 % Cd.

Initially water leaching tests were performed at various conditions of leaching temperature, reaction time and particle size. The optimized conditions for water leaching were found to be 2 h, 95°C and 250 g/l pulp density with a final pH of 5.9. However, the zinc recovery value of 10.26 % was not adequate for industrial scale operations itself.

In acid leaching trials; acid concentration, temperature, reaction time and particle size were the chosen variables. At the optimized condition of 150 g/l $H_2SO_4$, 95°C, 2 h at 250 g/l pulp density with a final pregnant solution pH of 4.2, the extraction values were determined as 74.87 % for Zn and 39.59 % for Fe.

These recovery values were evaluated as suitable for industrially feasible operations while creating a secondary leach residue of a composition of 4.10 % Zn, 19.17 % Pb, 5.52 % Fe and 85 ppm Cd that would not be suitable for pyrometallurgical lead production.

After recovering zinc in considerable amount by hot sulphuric acid leaching, NaCl leaching experiments for the extraction of lead were done on the secondary leach residue by taking temperature, time and pulp density into account. The most promising conditions of brine leaching for lead recovery were found as 300 g/l NaCl, 20°C, 15 minutes and 20 g/l pulp density that gave approximately 82 % lead recovery with a final residue of 7.87 % Pb, 6.86 % Zn, 8.79 % Fe.

Keywords: Recovery, Neutral Leach Residue, Leaching, Zinc, Lead

# ÖZ

# ÇİNKUR LİÇ ATIKLARINDAN ÇİNKO VE KURŞUNUN GERİ KAZANIMI İÇİN OLASI LİÇ PROSESLERİNİN İNCELENMESİ VE PROSES GELİŞTİRİLMESİ

Sunkar, Ahmet Semih

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Yavuz A. Topkaya
Ocak 2005, 87 sayfa

Bu çalışmada ana amaç % 12,59 Zn, % 15,21 Pb, % 6,45 % Fe ve % 0,054 Cd içerikli Çinkur nötr çözümlendirme artığı karışımından çinko ve kurşunun geri kazanımı için uygulanacak olan çeşitli liç yöntemlerinin incelenmesidir.

İlk olarak değişkenlerin sıcaklık, süre ve tane boyutu olarak seçildiği suda çözümlendirme deneyleri yapılmıştır. Su liçi sonucunda optimum şartlar olarak 2 saat, 95°C ve 250 g/l pülp yoğunluğunda son pH olarak 5,9 bulunmuştur. Ancak, belirlenen % 10,26 çinko randımanı endüstriyel uygulamalar açısından yeterli bulunmamıştır.

Suda çözümlendirme işlemlerinin tatminkar sonuç vermemesinden ötürü tesiste hazır bulunan sülfürik asitte çözme işlemleri çinko kazanımı için alternatif olarak düşünülmüştür. Optimal şartlarda (150 g/l $H_2SO_4$, 95°C, 2 saat, 250 g/l pulp yoğunluğu ve son pH 4,2) % 74,87 ve % 39,59 oranında çinko ve demir çözündürme randımanları bulunmuştur. Bulunan çinko liç verimi değerleri ekonomik olarak uygulanabilir değerler olarak kabul edilmiştir.

Belirtilen asitte liç şartlarında oluşan ikincil çözümlendirme artığında % 4,10 Zn, % 19,17 Pb, % 5,52 Fe ve 85 ppm Cd tespit edilmiş, ve artık pirometalurjik kurşun üretimi için yetersiz bulunmuştur.

Çinkonun sıcak sülfürik asitte çözdürülmesini takiben NaCl çözeltisinde liç edilecek ikincil liç artığından 300 g/l NaCl konsantrasyonu, 20°C liç sıcaklığı, 20 g/l pülp yoğunluğu ve 15 dakika sürede % 82'lik bir verimle kurşunun kazanılabileceği yapılan deneylerle belirlenmiştir. Oluşan nihai liç artığın kompozisyonu % 7,87 Pb, % 6,86 Zn, % 8,79 Fe olarak bulunmuştur.

Anahtar Kelimeler: Geri Kazanım, Nötr Liç Artığı, Liç, Çinko, Kurşun

*To My Mother & In Memory of My Father*

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# CHAPTER 1

# INTRODUCTION

The metallic zinc forms the II-B group of the periodic table together with cadmium and mercury. First use of zinc could be dated back to ancient times, and was used as alloying addition of brass by direct smelting of copper ores. Around 13th century, metallic zinc was first produced in India by reducing calamine with organics, i.e. wood or wool even though the word “zinck” first appeared in the work of Basilius Valentinus in Europe, during 15th century without any mention of metallic zinc. Generally, it is assumed that the real chemical isolation, or extraction, of metallic zinc was first achieved by Paracelcus in 16th century [1].

Lead, as a member of IV-A group of periodic table, exhibits quite significant properties that have been known and utilized for centuries by mankind. Archeological dating studies over lead bearing antiquities have proven that lead was known by Egyptians, Chinese and Romans at around 3800 B.C. in the use of glazing pottery, lining of tea chests and delivery of water. This is quite understandable as some of the minerals of lead can be reduced by coal (carbon monoxide) [2].

Zinc and lead have always been important base metals and utilized not only as metals but as additives in various fields. In the world, zinc and its associate lead, are produced in sequential ways in which pyro and hydrometallurgical methods may selectively be employed regarding the raw material.

In Turkey, there exists only one primary zinc plant, namely Çinkur. The plant was designed to process oxidized type zinc and lead ores and had been in operation for over 20 years until its shut down in year 2000.

The production method of the plant that will be explained further in the following chapters depended on waelz – leach – electrowin sequence with 40,000 t/y Zn and 6,000 t/y Pb capacity. Figure 1.1 plant overview can be seen.

Figure 1.1 – Overview of Çinkur Zinc and Lead Plant

During processing of the raw materials, following the waelz operation ground clinkers are treated in sulphuric acid where zinc is dissolved in neutral leach solution while leaving the insolubles as unaffected neutral leach residue which is simply the primary concern of this study.

In continuous operation period of the plant for over 20 years, the neutral leach residues have not been further treated for lead recovery at the already available short rotary kiln type pyrometallurgical lead production plant at Çinkur. To get an economically feasible lead extraction in short rotary furnaces, followed by a series of kettle refining soft lead bullion production operation, charge has to be blended with coke, flux making and $SO_x$ depressing additives like iron and $Na_2CO_3$.

Various trials have been applied to yield an economical route for processing of the already existing source, including concentration by blending of residue with lead ores and concentrates however, these attempts did not give satisfactory results because of the high threshold that limits the overall process economy. This constraint is the initial lead content of the charge that should be at least 40 % Pb. Therefore, due to poor recoveries and high treatment expenses to compensate the lead deficiency neutral leach residues of the zinc production step have been discarded in stockyards in vast amounts for many years. It has been estimated that 1,200,000 tons of dumped residue is present as heaps without the use of any preventative measures.

In fact, pollution potential of the dumped waste, due to weathering, was reported as very crucial, since the heavy metal content and readily soluble fraction under atmospheric conditions are above the permissible limits of the environmental regulations [3].

Therefore, to recover heavy metal content of the leach residues, thus to regain their economic value, and most importantly to reduce the severity of the environmental pollution risk, these residues must be treated by a suitable processing method that does not create toxic residues.

For the mentioned reasons, this study aims to find environmentally friendly metallurgical treatments that can recover already lost metallic values in the up most levels, or convert the residues to industrially treatable raw materials while leaving environmentally safe by-products or wastes. Furthermore, the proposed candidate processing technique(s) must comply with the current and future environmental regulations and possess low energy, reactant/solvent requirements.

Among the alternative metallurgical processes, at the start pyrometallurgical routes were discarded because of their intensive energy and fuel needs and special reactor requirements, which could result in high capital investment and hazardous gas emissions.

As a result, in the light of what has been claimed, it was considered to conduct experiments based on hydrometallurgical methods under different conditions. Residues were planned to be treated in water, sulphuric acid and sodium chloride solutions to investigate the dissolution performances of these media. In this study, it was also aimed to find methods that could be linked with ease to the already existing hydrometallurgical plant.

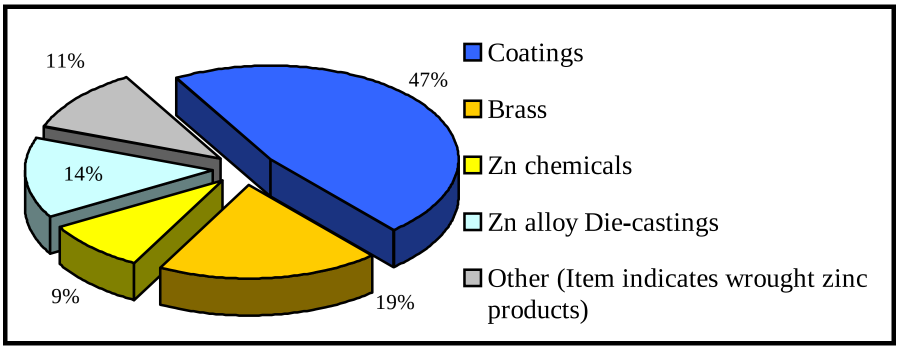
# CHAPTER 2

# THEORY AND LITERATURE SURVEY

## 2.1. Zinc and Lead in Applications

Zinc is the fourth most commonly used metal after steel, aluminum and copper in the world. Since it is chemically active, exhibits high tendency to form compounds with other elements; consumption of the metal and its alloys has increased. In consequence of its chemical properties, major application fields can easily be anticipated and be listed as galvanizing or coating industries of base metals, die casting of zinc alloys production of brass and paint pigments production for chemical industries. Surveys conducted emphasize the importance of the metallic zinc that is expected to increase if current economic status and development sustain [4].

Primary metallic zinc is mostly consumed by following industries even though there are several other fields. From Figure 2.1 an outline of the consumption and relative importance by industries can be seen [5].



Source: ILZSG (UN International Lead Zinc Study Group) [4]

Figure 2.1 – Proportions of World Metallic Zinc Consumption

### 2.1.1. Zinc in Base-metal Coatings

Some metals, especially iron and steel, are prone to corrosion so they are coated by more electropositive elements like zinc. In these applications, the foremost reasons for zinc employment are its oxides' high resistivity to chemical decomposition and its application economy.

Zinc coating methods can be given as follows:

i. Hot dip galvanizing
ii. Electrogalvanizing
iii. Metallizing – spraying with molten zinc droplets
iv. Sherardizing

### 2.1.2. Zinc and Zinc-based Alloys in Castings

Zinc alloys are classified as zinc-based alloys and alloys where zinc is an additive. The most important area that consumes zinc is brass production after coating applications. Although brass is known as copper-zinc alloy, some other constituents are commonly present, depending on the required mechanical properties of the final product. Brasses are widely used in construction, machinery, telecommunication and information technology sectors and in welding electrode manufacturing.

Zinc-base alloys containing more than a small percentage of copper, nickel, iron, magnesium, chromium, titanium, etc. cannot be worked satisfactorily. Furthermore, low melting and boiling temperatures of zinc and its alloys trigger die-casting method. Consequently, some complex parts and/or specialty alloys can be given shape by utilizing close dimensional control feature of die-casting method for which zinc die-casting alloys are used. The most famous ones are Zamak™ and battery alloys that generally contain 4 % Al.

### 2.1.3. Zinc Chemicals and Compounds

Comments on the chemical nature of the elemental zinc can give significant clues about the properties of its compounds and their applications. Strong electropositivity is the basis for its chief commercial use in previously mentioned industries. Important zinc compounds and their common employment fields are given in Table 2.1 [4].

Table 2.1 – Fields of Use of Common Zinc Compounds/Chemicals

| Compound | Formula | Field of use |
|---|---|---|
| Zinc sulfide | $ZnS$ | Lithopone and phosphors manufacturing |
| Zinc sulfate | $ZnSO_4$ | Nutrition to soil in agriculture |
| Zinc acetate | $Zn(C_2H_3O_2)_2$ | Caustic in dyeing, preservative in wood industries |
| Zinc borate | $ZnO.B_2O_3$ | Fire retardant of fabrics |
| Zinc carbonate | $ZnCO_3$ | Paint pigment in pharmaceuticals |
| Zinc chromate | $ZnCrO_4$ | Corrosion inhibiting primer |
| Zinc cyanide | $Zn(CN)_2$ | Electroplating |
| Zinc halides | $ZnF_2$ | Galvanizing, wood industries and ceramics |
|  | $ZnCl_2$ | Wood preservative, fungicide, dehydrater |
|  | $ZnCl_2.2NH_4Cl$ | Flux for etching, welding and soldering |

Source: ILZSG [4]

Among the zinc compounds zinc oxide is the most important industrial chemical, with respect to its total tonnage and value. Major fields of use of zinc oxide are very diverse; however, some of them are dominant and need mentioning. In rubber industry $ZnO$ is used as activating agent for vulcanization treatments, in protective and decorative coatings used as white color bearing pigments. Moreover, in ceramics industry with its low coefficient of expansion gives ceramic bodies elasticity and thermal and mechanical shock resistivity. In addition, it is used as flux to decrease the softening points of ceramic bodies while keeping the color unaltered as having a neutral color. Besides, $ZnO$ is utilized in miscellaneous areas like in textile industry, in military applications as chemical smoke producers or lubricants.

Although not given amongst the zinc compounds, zinc dust is worth noting in this part, as its use is much closer to chemicals and compounds. While in iron and steelmaking processes zinc dust is undesired in other extraction processes zinc dust is vital. Considerable amounts of zinc dust are spent for extraction of other metals at following hydrometallurgical processes.

- Cadmium extraction from lead baghouse dusts
- Gold and silver extraction from cyanide solutions
- Precipitation of heavy metals in processing scrap
- Electrolyte purification

### 2.1.4. Lead in Applications

By noting important basic properties of lead, as listed below, one can forecast the potential use of lead.

- High corrosion resistance especially under atmospheric conditions
- Excellent anti-friction properties
- Low melting with high boiling point
- High scrap and re-use value (can repeatedly be recycled)
- Resistance to short wavelength radiation
- High workability, softness, specific gravity, conductivity with good weldability

If above properties are of main concern lead can be used for many applications where fatigue life and tensile strengths are not crucial. Main fields and relative proportions of lead use are listed below and presented in Table 2.2 [4]:

- Battery production
- Chemicals for petroleum refinery, rubber production and insecticides and gasoline additive as lead ethylene and/or methylene for octane regulation
- Pigments for glazes in ceramic industry, anti-corrosion oxide paints for marine applications
- Corrosion prevention isolation of underground transmission cables

- Radiation shielding in high-energy radiation fields
- Electrical condenser production in the form of foils with 0.01 mm thickness

Table 2.2 – Fields of Use of Lead and Their Relative Proportions

| Field of Use | Relative Use (%) |
|---|---|
| Battery | 60 |
| Alloys and wrought products | 12 |
| Chemicals and pigments | 13 |
| Cable isolation | 5.5 |
| Ammunition | 2.5 |
| Other | 7 |

Source: ILZSG [9]

Among the above applications, the foremost one is as can be guessed battery production. For automotive batteries, high capacity electrical storage applications, and high technology long-lasting communication systems uninterrupted stable energy supply is extremely necessary. Since cell voltage and lifetime of the batteries are directly related to the quality of the lead plates, during production of battery lead to get a hard, resistant and high surface quality plates, pure lead is alloyed with antimony, calcium, tin and/or arsenic. Antimony and calcium give required wear resistivity and hardness when 6 – 12 % is added to lead, whereas tin and arsenic is added to reach a better surface quality [6].

## 2.2. Occurrence of Zinc and Lead

Occurrence, mineralogy, geology and process economy of all metals and minerals are very important in evaluating the feasibility of the metallurgical processes; therefore, it is better to note these points in this section.

Zinc and lead ore deposits are distributed widely throughout the world despite about 50 % of them being located in three countries as Australia, Canada, and the U.S. (Table 2.3 and Table 2.4). These metals, like several others, tend to occur in delimited areas called “metallogenetic provinces”. For example, in North America, such provinces lie along the eastern coast starting from Tennessee through Virginia, New Jersey and reach New Foundland at the north. In Europe, a smaller province can be found through Alpine ranges between France and Serbia & Montenegro. In Africa, moreover, provinces lie along Northern coast starting at Morocco and end at Tunisia [7].

Table 2.3 – Zinc Mine Productions, Deposits and Reserves of Leading Countries

| **Countries** | **Mine Production** (x 1000 t) | | **Reserves** (x 1000 t) | **Estimated Reserves** (x 1000 t) |
|---|---|---|---|---|
| | **2002** | **2003** | | |
| USA | 780 | 770 | 30,000 | 90,000 |
| Australia | 1,150 | 1,600 | 33,000 | 80,000 |
| Canada | 894 | 1,000 | 11,000 | 31,000 |
| China | 1,550 | 1,700 | 33,000 | 92,000 |
| Mexico | 475 | 500 | 8,000 | 25,000 |
| Peru | 1,100 | 1,250 | 16,000 | 20,000 |
| Others | 2,410 | 2,650 | 59,000 | 87,000 |
| **World Total** | **8,360** | **8,500** | **220,000** | **460,000** |

Source: USGS [11]

Table 2.4 – Lead Mine Productions, Deposits and Reserves of Leading Countries

| **Countries** | **Mine Production** (x 1000 t) | | **Reserves** (x 1000 t) | **Estimated Reserves** (x 1000 t) |
|---|---|---|---|---|
| | **1999** | **2000** | | |
| USA | 499 | 490 | 21,000 | 27,000 |
| Australia | 633 | 700 | 16,000 | 28,000 |
| China | 560 | 570 | 2,000 | 3,000 |
| Peru | 267 | 270 | 2,000 | 3,000 |
| Canada | 159 | 147 | 12,000 | 17,000 |
| Mexico | 130 | 140 | 3,000 | 4,000 |
| Sweden | 123 | 121 | 1,500 | 2,000 |
| Others | 598 | 661 | 43,500 | 54,000 |
| **World Total** | **2,979** | **3,101** | **101,000** | **138,000** |

Source: USGS [10]

In Turkey particularly, zinc and lead are found in Zamantı and Bolkarlar areas in Central Anatolia and between Balya and Handeresi in the west as smithsonite. (Figure 2.4) Along Eastern Black Sea shore, along with copper, lead and zinc are excavated as sulphides in considerable amounts. Turkish zinc and lead ore reserves varying in chemical composition and properties because of small sizes of the mines whose average reserves are around 30 – 60 thousand tons of metallic zinc or lead. Furthermore, for ordinary zinc ore bodies of the Central Anatolia ore basin, it can be claimed that commercially important reserves are in the form of carbonates with siliceous gangue, their diversity is because of associated and gangue minerals of each different mineral layer. For lead ores, on the contrary, along Black Sea shore and Western Anatolia region deposits have 95 % sulphidic lead ore bodies with associated zinc and copper minerals [8,9].

Zinc and lead deposits of Turkey constitute 1.7 % and 2.4 %, respectively, of the estimated reserves of the world. When these values are compared with land area, that is 0.53 % of that of the world, Turkish reserves can be regarded as reasonably rich when considered together with already present cadmium.

Surveys of USGS on annual world zinc and lead production breakdown with respect to continents are shown in Figures 2.2 and 2.3 [10,11].

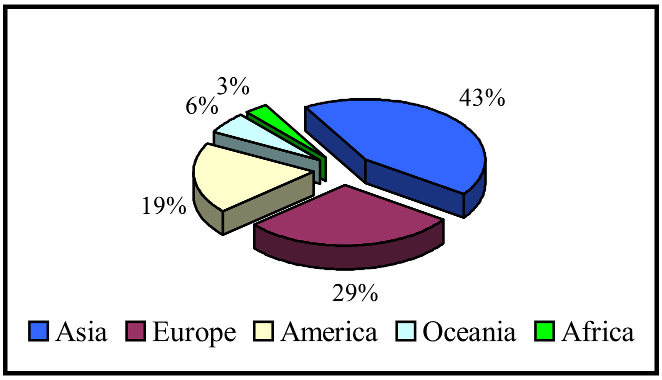


Figure 2.2 – Relative Zn Productions of Continents

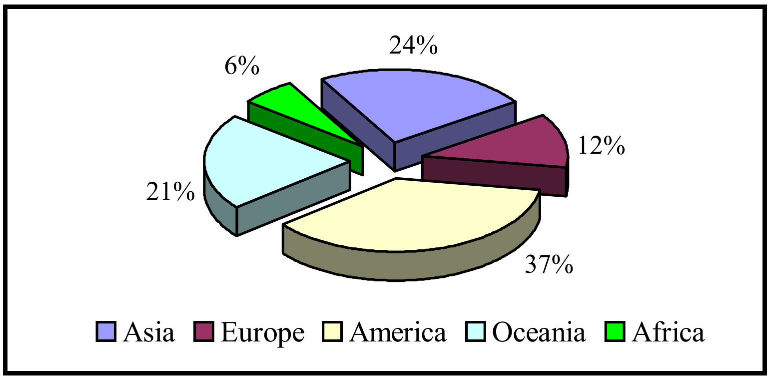


Figure 2.3 – Relative Pb Productions of Continents

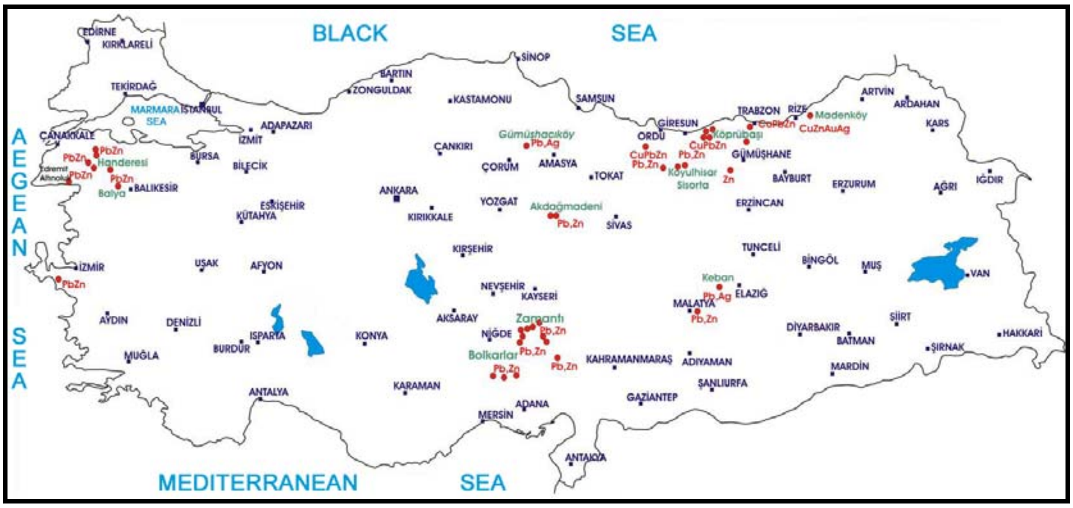


Figure 2.4 – Map of Some Important Zinc and Lead Ore Deposits of Turkey [7]

The mineralogy of zinc is not complex as there are only 7 commercial minerals of which sphalerite (ZnS) is the most important and other minerals are derived from it by weathering as smithsonite and calamine [1]. (See Table 2.5)

Sphalerite, in nature, can rarely be found alone; it is mainly associated with lead minerals, galena (PbS), cerussite ($PbCO_3$) and anglesite ($PbSO_4$). Besides, most of the world's cadmium production originates from zinc ores and Cd is produced as a by-product of zinc. Other common associated minerals are chalcopyrite ($CuFeS_2$) and pyrite ($FeS_2$).

Other valuable metals can also be found in ore structure and add considerably to the value of zinc. Gold, silver, germanium, indium and thallium can be produced as by-products from zinc ores.

Conversely, lead mineralogy is not as simple as zinc mineralogy. Lead minerals can be rather complicated as lead has quite higher affinities to form intermetallics. Furthermore, minerals are classified according to the rock bodies to which they bound. For this reason, it would be convenient to mention only the commercially most important minerals and their derived forms. (See Table 2.6)

Table 2.5 – Industrial Minerals of Zinc

| Mineral | Chemical Formula | Weight % Zn |
|---|---|---|
| Sphalerite, zinc blende (wurtzite) | $ZnS$ | 67.0 |
| Smithsonite | $ZnCO_3$ | 52.0 |
| Hemimorphite (Calamine) | $Zn_4Si_2O_7(OH)_2.H_2O$ | 54.2 |
| Hydozincite | $Zn_5(OH)_6(CO_3)_2$ | 56.0 |
| Zincite | $ZnO$ | 80.3 |
| Willemite | $Zn_2SiO_4$ | 58.5 |

Table 2.6 – Industrial Minerals of Lead

| Mineral | Chemical Formula | Weight % Pb |
|---|---|---|
| Galena | $PbS$ | 86.6 |
| Cerussite | $PbCO_3$ | 77.5 |
| Anglesite | $PbSO_4$ | 68.3 |
| Pyromorphite | $Pb_5Cl(PO_4)_3$ | 50.3 |
| Jamesonite | $Pb_2Sb_2S_5$ | 76.4 |

In common zinc and lead ore bodies, calcite ($CaCO_3$) and dolomite ($CaMgCO_3$) comprise the gangue material portion together with less common quartz ($SiO_2$). Other possible gangue minerals are rhodochrosite ($MnCO_3$), barite ($BaSO_4$), and fluorspar ($CaF_2$) that can be further processed for recovery as by-products.

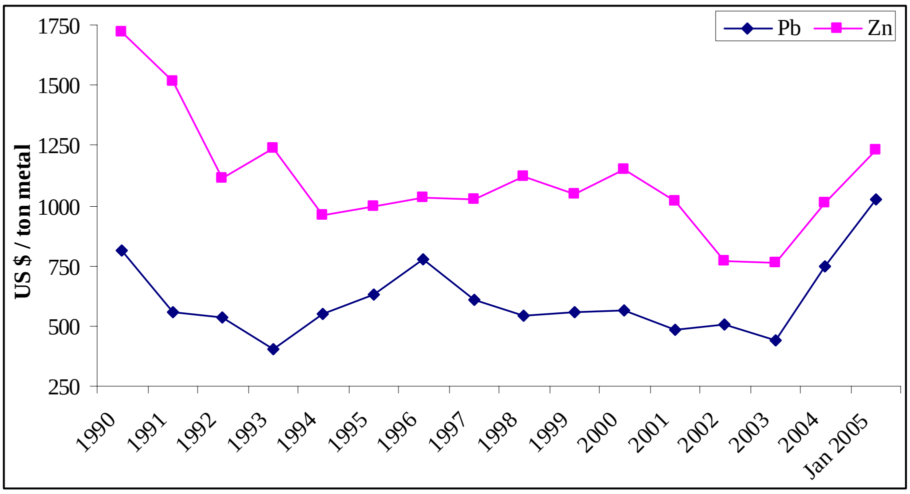


Figure 2.5 – Average Annual Prices of Pb and Zn between 1990 and 2005

Metallic zinc and lead prices have been in fluctuating trend since late 1980s. These trends in annual metallic lead and zinc prices were given in Figure 2.5 [12].

## 2.3. Production Methods of Zinc and Lead from Primary Sources

Major production techniques of zinc and lead vary a lot. The global production of zinc is mostly dependent on electrolytic extraction even though some of the zinc is produced by pyrometallurgical routes that are not as common and efficient as hydrometallurgical ones. However, for lead, pyrometallurgy is the leading treatment method. Although some efforts towards hydrometallurgical processing resulted in promising results, they have not been found feasible for industrial applications.

### 2.3.1. Extraction of Zinc

#### 2.3.1.1. Pyrometallurgical Extraction

From Figure 2.6, as can be understood, the use of pyrometallurgical processes is not as wide spread as hydrometallurgical treatment; however, vertical retort and imperial smelting processes (ISP) keep their importance and are worth being mentioned in this section [13].

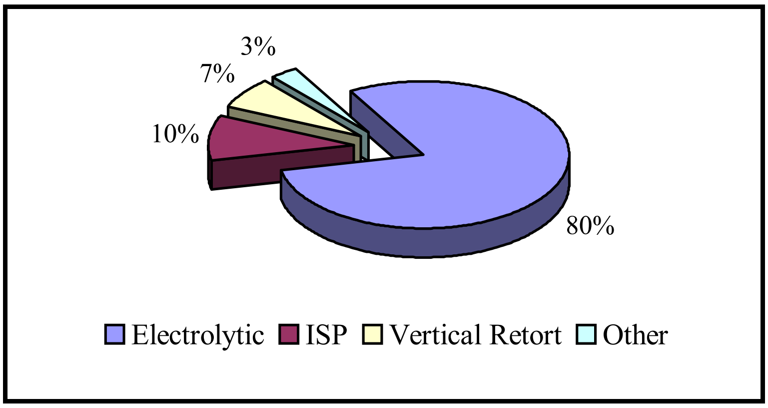


Figure 2.6 – Relative Use of Zn Production Methods

##### 2.3.1.1.1. Vertical Retort Process

The basic principle in vertical retort processing is that by reducing action of coke, ZnO is converted to Zn fume that is separated from $CO_{(g)}$ and collected at condensers before being oxidized. Reduction takes place according to reactions (1) and (2).

$$ZnO_{(s)} + CO_{(g)} \rightarrow Zn_{(g)} + CO_{2(g)} \qquad (1)$$

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)} \qquad (2)$$

The required heat for reduction of ZnO at 1300°C is simply supplied by burning of coke according to reaction (2). The burden that is composed of zinc bearing concentrate, flux and coal is fed into the furnace at predefined intervals as if in blast furnace operations, and yields continuous metal production and spent briquettes that are taken from reactor area by a slowly rotating drum extractor. Spent briquettes can contain as mush as 30 % C, 3 % Zn and other trace metals thus are burned as fuel for heating boilers.

Zinc metal vapor is separated from gaseous phase at splash-condensation chamber, which is severely agitated to attain the highest rate of liquid droplet formation so that flue gases and CO leave the system as gases with minimum zinc loss since it can easily be re-oxidized to ZnO [14].

#### 2.3.1.1.2. Imperial Smelting Process

ISP is designed on the basis of blast furnace technology that is still being used for lead smelting. In this method, like blast furnace, the carbonaceous fuel, lead and zinc bearing ores or concentrates are first agglomerated to withstand the extreme working conditions of the reactor. Afterwards, the agglomerated charge is fed into furnace where coke reduces zinc or lead oxide to metal.

Zinc and a small portion of lead vaporize upon heating and resultant gas is condensed and partially distilled at off-take end of the furnace in splash condensers that help to obtain zinc metal. Some considerable amount of zinc is re-oxidized and lost while taken off the system at splash condensers. After condensation, gases are further treated (cleaned, dried) to recover lost zinc or blue powder. Lead, on the other hand, is taken from the furnace at its hearth region by tapping the liquid metal layers [15].

### 2.3.1.2. Hydrometallurgical Extraction

Being the most widely used production method for zinc, hydrometallurgy needs to be explained further in detail. Hydrometallurgical extraction of zinc can be considered in two sub-sections as direct and indirect routes.

#### 2.3.1.2.1. Production from Zinc Sulphide Ores

Sphalerite containing ores, can be processed by both direct and indirect methods. In direct method, the procedure starts with ore preparation by communition and beneficiation and then the concentrate obtained is sent to autoclaves which is oxygen pressurized to leach sulfides instead of utilizing roasting as a pretreatment process as seen in Figure 2.7.

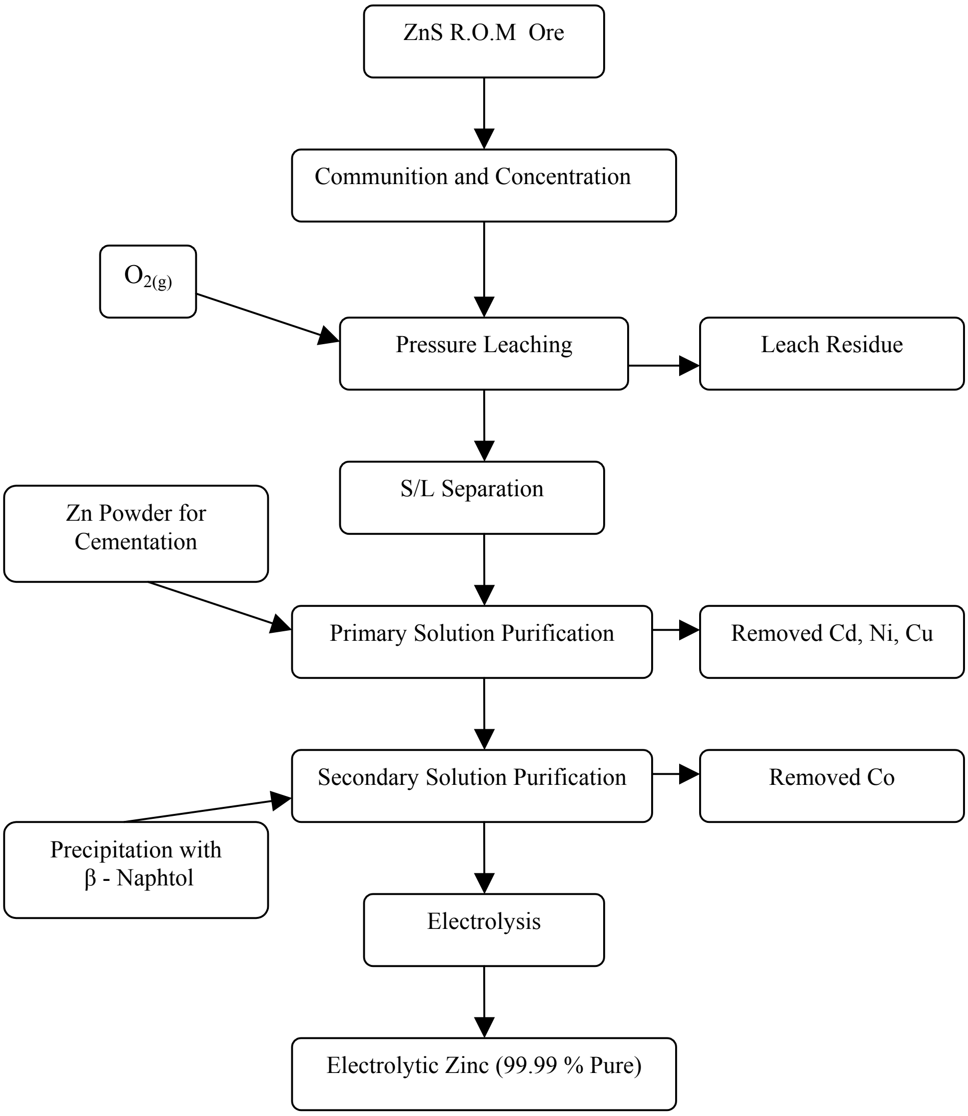


Figure 2.7 – Pressure Leach – Electrowin Treatment of Sulphidic Ores

In indirect hydrometallurgical technique, on the other hand, basically, ores or concentrates are subjected to oxidative roasting to convert diluted sulphuric acid insoluble ZnS to soluble ZnO and to increase metal concentration of the raw materials by forcing sulphur to react with oxygen to yield $SO_x$ gases.

Principle reactions of this process, under predefined temperature and oxygen partial pressure, are:

$$ZnS_{(s)} + 3/2O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)} \tag{3}$$

$$2SO_2 + O_2 \rightarrow 2SO_3 \tag{4}$$

$$ZnO + SO_3 \rightarrow ZnSO_4 \tag{5}$$

During roasting most of the iron present in the concentrate reacts with ZnO to form insoluble zinc ferrite under normal leaching conditions. Preferential or selective roasting can be a remedy to eliminate zinc ferrite formation but there is no way of completely avoiding this problem as roasting is carried out at about 900°C that is usually chosen in practice [16]. On the other hand in pyrometallurgical treatment of zinc concentrates, zinc ferrite formation is not so critical as it can be reduced by carbothermic reduction.

The major part of the zinc calcine is treated in neutral leach step. Here an excess of calcine is treated with the solution from the subsequent acid leach and with some return electrolyte. Because of the excess of ZnO, the pH of the solution after leaching will be around 5 [17].

At this pH any iron and aluminum that had come from the acid leach will precipitate as hydroxides together with silica and absorbed arsenic and antimony. The solids are separated from the solution by settling and filtration. In addition to the precipitates, solids containing an excess of zinc calcine are treated by acid leaching.

In the acid and neutral leach steps a good contact between the liquid and the finely divided calcine is required. The zinc oxide calcine which is finely wet ground to –

44 microns in a closed circuit, is added to an agitation type leach tank. Processes are usually carried out in Pachuca tanks. The pulp continuously overflows into the subsequent settlers or Dorr thickeners.

Removal of cobalt and chlorine is not always required. Cobalt and chlorine are extracted from a portion of electrolyte (temporarily removed from the circuit) to avoid their accumulation above a given level. The purified neutral zinc sulfate liquor with a pH of around 5 is electrolyzed as seen in Figure 2.8.

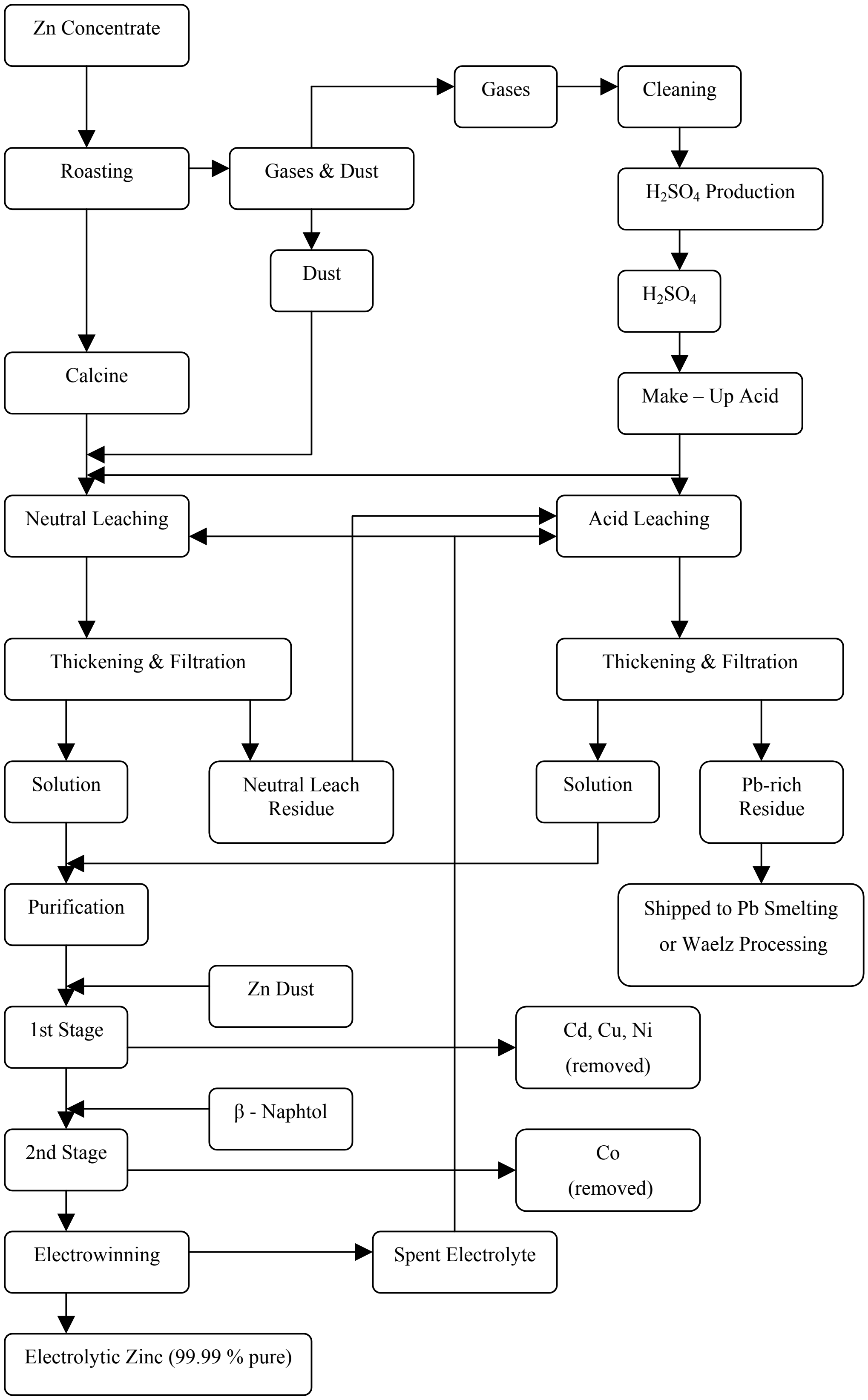


Figure 2.8 – Roast-Leach-Electrowin Treatment of Sulphidic Concentrates with Simultaneous Treatment of Neutral Leach Residue

#### 2.3.1.2.2. Production from Zinc Carbonate Ores

In the world as mentioned above as a main source of zinc, sphalerite mineral either in ore or concentrate form is preferred economically. However, due to high reserves, in Turkey zinc carbonate ores containing smithsonite ($ZnCO_3$), have been preferred for years. Carbonate ores, not like sulfide ores, are not easily floated by the addition of sulphurophilic surfactants hence their concentration depends on the chemical conversion of primary raw material by pyrometallurgical pretreatments other than roasting. Although this treatment is assumed as pretreatment process, it is a must for hydrometallurgical treatment of carbonate ores of zinc.

Waelz kilns, rotary kilns of an average length of 70 m and a diameter of 4.5 m reactors, are employed to reduce $ZnCO_3$, by coke and lime at about 900 – 1300°C, to give metallic Zn vapor which consequently oxidized by air in kiln space and/or at coolers of rotary kiln to ZnO. Waelz oxide with a composition of 55 – 65 % ZnO, is collected by bag filters and sent to densifying kilns. Densification process is applied at 900 – 1100°C interval where volatile elements Cl, F, Pb, and Cd are taken off to a high extent from the oxide [18]. Then, the clinker is cooled and sent to a dry grinding unit to prepare these clinkers for leaching.

The ground clinkers are sent to a series of leach tanks containing $H_2SO_4$ solutions of 180 – 200 g/l, having different pH values that rise from the first to last due to the dissolution of ZnO in solution. Calcine and some fresh make-up acid additions are done to first tank, solution overflows to next tank for further dissolution.

At the end of leaching at a temperature of 80 – 90°C, the obtained pulp is sent to thickening and filtration. Purification of zinc sulfate solution and electrowinning of zinc are similarly done as explained above without any considerable variation from sulfide concentrate treatment as seen in Figure 2.9.

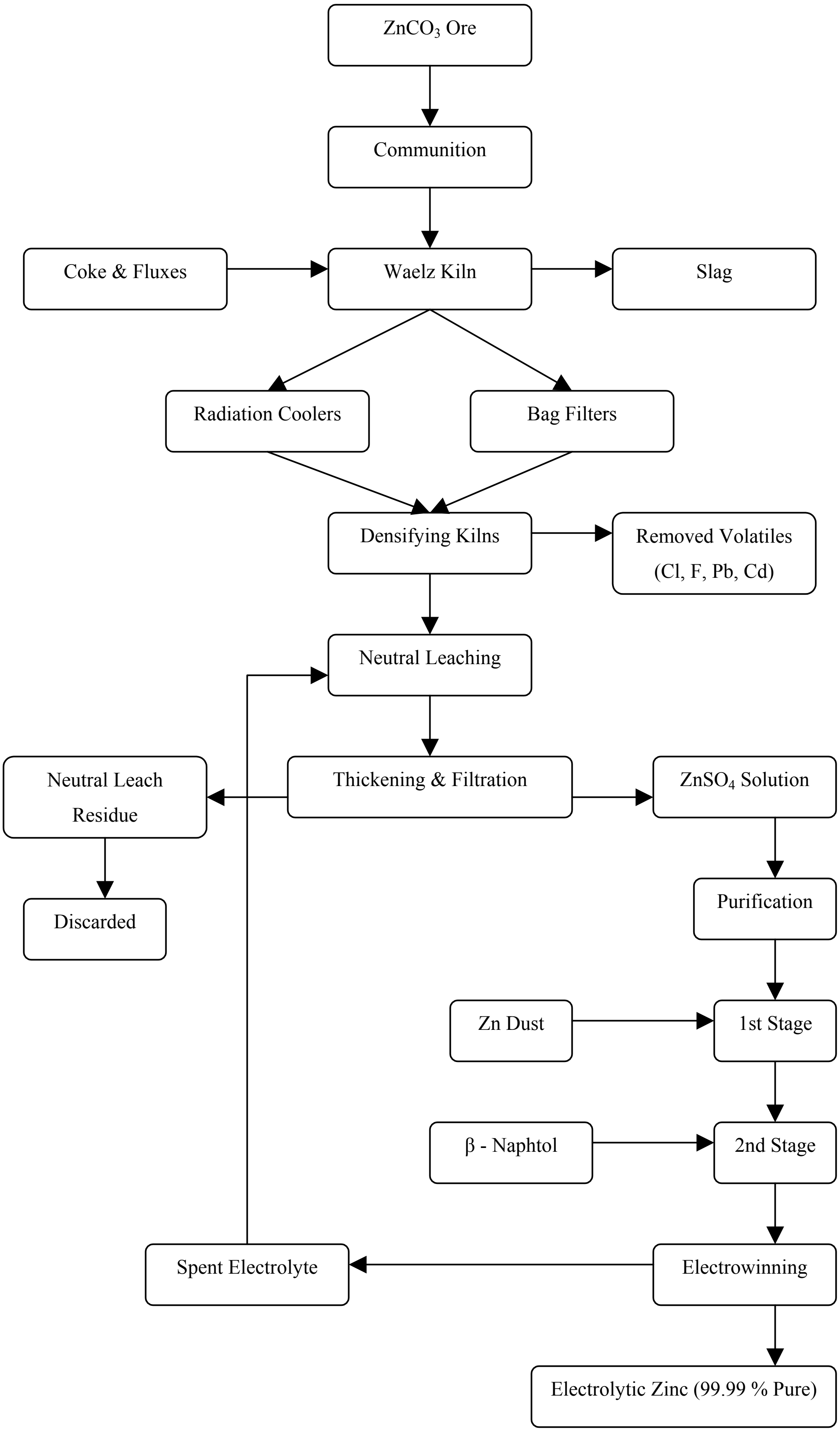


Figure 2.9 – Waelz-Leach-Electrowin Treatment of Carbonate Ores

## 2.3.2. Extraction of Lead

### 2.3.2.1. Pyrometallurgical Extraction

Pyrometallurgical treatment of lead can be divided into two sub-sections; continuous and batch processes.

#### 2.3.2.1.1. Continuous Processes

Continuous processes are mostly achieved by using shaft type furnaces namely ISP, blast furnace and vertical retorts. For all these three methods, the principle source of lead is galena (PbS), which usually arrives at smelters in the form of finely divided flotation concentrate containing Fe, Cu, Zn, Ag, Au, As, Sb, Bi and Sn. Before smelting in ISP, lead blast furnace, or vertical retorts, impurity-containing concentrate is subjected to reactive sintering where roasting for PbS to PbO conversion and agglomeration of finely disseminated concentrate to coarse-grained sinter are done at the same time.

All types of shaft furnace smelting operations necessitate uniform particle distribution, strength and gas permeability. For this reason, concentrate is fed to Dwight-Lloyd type sintering machine together with appropriate fluxing and binding additives. Required heat in sintering is supplied by exothermic oxidation reaction of galena.

In the blast furnace, lead oxide is readily reduced by carbon at oxygen potentials where most of the iron goes into the slag phase or it combines with sulphur to form a matte phase. At the same time, another phase, Speiss, which is a solution of arsenides and antimonides, can form along with matte, almost pure lead and silicate-rich slag at the hearth of the furnace. All these four layers are practically immiscible and let be drained [14].

Blast furnace lead can contain small amounts of base-metal impurities such as As, Sb, Sn, Bi, and Cu…etc. that should be removed before lead is in its final product form.

Furthermore, the presence of valuable precious metals (Ag, Au) needs further refining to recover them as by-products. Normally, commercially pure lead production has several refining and fire refining steps, shortly;

- Softening for As, Sb, Sn removal by oxygen
- Desilverizing by Zn
- Dezincing
- Debismuthing by Ca or Mg

QSL (Queneau – Schuhmann – Lurgi) process was developed as an alternative continuous process to ISP regarding the process flexibility and composition of the raw materials. Process was designed to convert lead sulphide into metallic lead by avoiding complete oxidation. The products are metallic lead and lead oxide as there exist partial oxidation of the raw materials. The lead oxide is taken off the system in the slag phase that is reduced by carbon to get metallic lead. Almost 75 % of the Pb content of the burden can be recovered as metallic lead while most of the remaining portion enters the slag phase. Since slag contains approximately 70 % Pb and it is processed, the actual recovery values are higher.

From the zinc production point of view, QSL can be considered as long as there is enough sulphur in the burden for autogeneity of the process. However, low zinc containing materials can also be processed in a supplementary step that handles the secondary slag formed during reduction of primary slag phase. Moreover, the process is promising in terms of off gases since it produces low volume off gases at high $SO_2$ content and temperature (1100°C), acid production and waste heat regeneration become possible.

#### 2.3.2.1.2. Batch Processes

Several processes have been developed in order to treat sulphidic concentrates together with lead oxide based residues. These developments have been derivations of BOF steelmaking treatment to lead containing charge material. The most important batch processes are:

- Ausmelt
- Kaldo process
- Kivcet process

### 2.3.2.1.2.1 Ausmelt® Process

Ausmelt® process was developed in Australia by using SIROSMELT® lance technology that permits injection of process gases underneath the melt surface without using cooling water. High-speed gases are utilized to give necessary cooling rates before dissociation of lance in melt.

The pumped gas creates intensive stirring effect that enables complete combustion of inexpensive fuels. Ausmelt furnaces are versatile to be used in smelting, reduction or slag fuming, they do not require oxygen and rotation, and waste heat recovery is possible. Due to stationary usage of furnace, the lead production is continuous but for industrially continuous operation, there should be at least three furnaces in series.

### 2.3.2.1.2.2. Kaldo® Process

Kaldo® is a process that is based on a steelmaking process developed in Sweden. It was adopted by Boliden AG, mining and smelting company, to treat secondary Pb materials and dusts in late 70s. It has been developed to process Cu secondaries and has been utilized to produce lead from primary sources practically.

Kaldo uses a rotating vessel to give good heat transfer and mixing with a water-cooled lance in the furnace but not in the bath to provide heat. It is very much similar to Top – Blown Rotary Converter in principle, has a limited capacity and is a batch process which produces dilute $SO_{2(g)}$ concentration discontinuously thus, makes $H_2SO_4$ production improbable.

Moreover, as process economy is important, some additional expenses should be predicted. For example, furnace linings cannot be cooled due to rotation of furnace and must be replaced in short time intervals and process is only autogenous when S % of charge is high hence requires extra fuel for complete reduction at predefined temperatures.

### 2.3.2.1.2.3. Kivcet® Process

Kivcet® is a Soviet technology, developed as flash smelting to produce copper and then adapted to produce Pb from sulfide concentrates using technical oxygen. An integral electric furnace is used to complete the reduction of lead oxides formed and provide some thermal balance to the system.

Although the process was investigated by many producers during early 1980s, the only plant was built in Italy operating with sulfidic Pb concentrates and some zinc plant residues of high oxide type Pb content. It is a process with low off gas of high $SO_2$ content [19].

### 2.3.2.2. Hydrometallurgical Extraction

In metallic lead production, emission of $SO_x$ gases limits the expansion of the industry, as environmental regulations are getting stricter; thus, many hydrometallurgical processing methods have been studied. Although there have been some experimental and pilot plant trials for hydrometallurgical techniques, industrially none of them has been found effective.

In one of these attempts, ferric chloride leaching of sulphide concentrates was experimented. The leach liquor is crystallized and centrifugally dried to get $PbCl_2$ that is then sent to fused salt electrolysis as seen in Figure 2.10. [17].

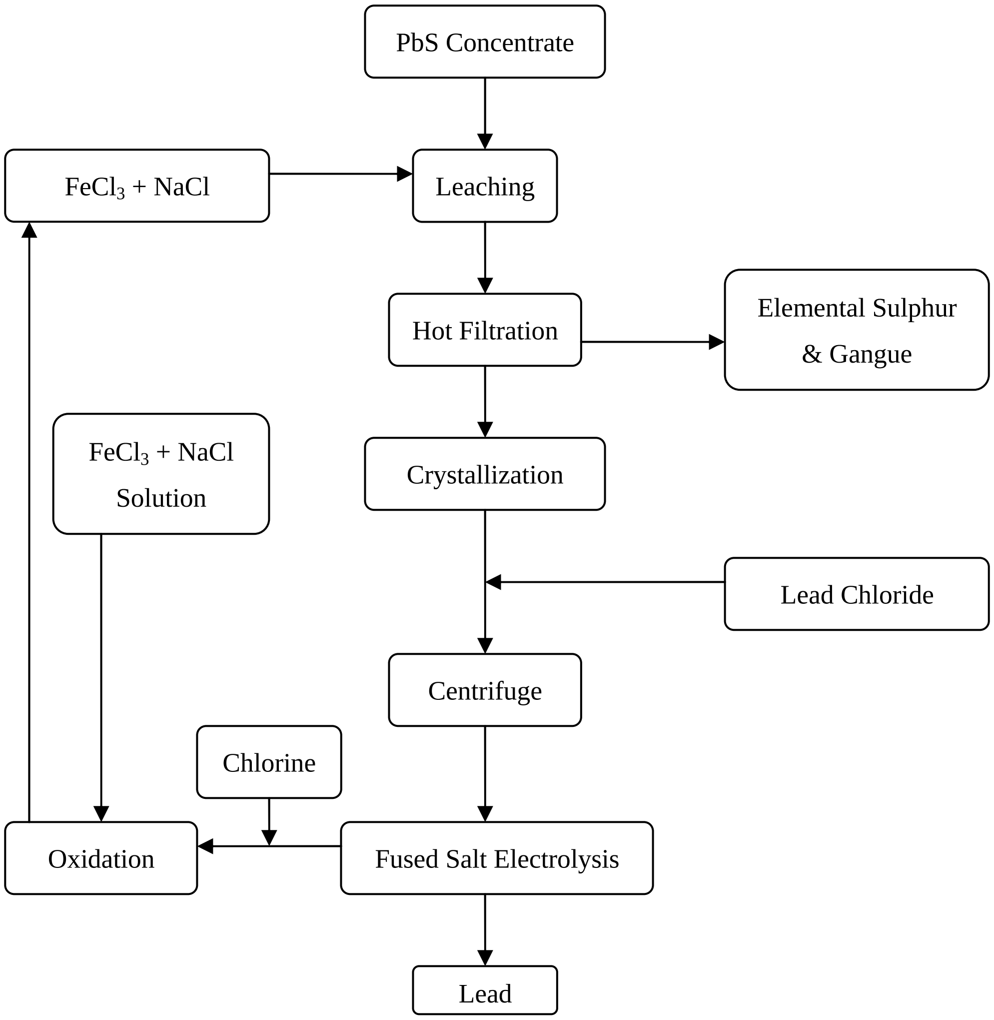


Figure 2.10 – Ferric Chloride Leach-Electrowin Treatment of PbS Concentrate

## 2.4. Recycling of Lead and Zinc

Recycling, a significant factor in the supply of many of the key materials consumed in our society, provides environmental benefits in terms of energy savings, reduced volumes of waste, and reduced emissions associated with the energy savings. Recycling is an increasingly important component of economic activity in the world. For instance, the estimated value of nonferrous metals, recycled in the US, in 1995, was about $11.5-$12.0 billion [20].

Once production route of any metal is compared to obtain commercially pure metal, production from secondary sources becomes much preferable when energy efficiencies, waste handling and environmental consciousness are concerned.

For all metals, when production from primary raw materials is considered there have always been following problems:

- Stability of mining area
- Availability of physically and chemically consistent ores or concentrates
- Transportation of ore or concentrate
- Contamination of water resources by toxic wastes therefore handling of wastes

On the other hand, reuse of secondary sources

- Minimizes or totally eliminates problems of mining site
- Ensures the physical and chemical consistency of sources
- Reduces transportation expenses as wastes exist in the plant yard
- Reduces the amount of waste and thus decreases the dumping area requirements with lowered pollutant contamination

For zinc, the recycling issue is more vital than other metals as 75 % of its consumption is in metallic form and half of which is used in galvanizing industry that requires higher treatment efforts to obtain desired quality.

For zinc compounds zinc oxide is the most crucial one with its consumption in agricultural, chemical, paint, pharmaceutical, and rubber sectors of the economy.

In year 2002, about 30% of world zinc was produced through secondary recovery. The main sources for secondary zinc are brass, galvanizing residues, die-casting scrap, zinc sheet and flue dust from electric arc furnaces (EAF). According to USGS surveys one fourth of the entire zinc consumption stems from secondary zinc recycling that is around 370,000 tons annually. Sources and relative shares of them in recycling of secondary zinc can be seen in Table 2.7.

Table 2.7 – Relative Proportions of Secondary Zinc Sources

| Sources | Relative Shares in Use (%) |
|---|---|
| Brass scraps | 32 |
| Galvanizing dross | 23 |
| Die-casting scrap | 16 |
| Zinc sheet | 10 |
| EAF flue dust | 8 |

About 2 % of recycled zinc was derived from new scrap, generated in galvanizing and die-casting plants, brass mills, and manufacturing facilities where basic zinc materials were consumed. New scrap consisted mostly of drosses, skims, furnace dust, residues, and clippings from the processing of galvanized steel sheet and strip, rolled zinc, and brass sheet. The other 20 % of recycled zinc was obtained from old scrap, which consisted almost entirely of die-castings (mainly from scrapped automobiles), brass products, and rolled zinc articles such as gutters, roofing, and engraving plates.

Recovery of zinc from the burning of tires for energy is small. However, increased zinc recovery from energy-generating tire burning and from recycling of carbon-zinc and alkaline battery appear to be other sources for near future gains in secondary zinc output. Table 2.8 indicates the differences in recycling periods of various products.

Table 2.8 – Recycling Periods of Some Common Zinc Products

| Product | Field of use | Recycling period (Year) |
|---|---|---|
| Zinc sheet | Roofing, Coating | 100 – 200 |
| Brass products | Wide range | 10 |
| Galvanized sheets, castings and strips | Automotive, machinery, roofing | 10 – 25 |
| Zinc compounds | Rubber tires | 1-25 |

Because of wide differences in the character and zinc content of scrap, the recycling processes of zinc-bearing scrap vary widely. Clean new scrap, mainly brass, rolled zinc clippings, and rejected die castings, usually requires only remelting.

In the case of mixed nonferrous shredded metal scrap, zinc is separated from other materials by hand or magnetically. Most of the zinc recovered from EAF dust produced during remelting of galvanized steel scrap is recovered in rotary kilns by using the Waelz process.

For lead, meanwhile, recycling ratio is higher than that of zinc, about 81% of the 1,370,000 tons of refined lead produced in the US, in 2002, was recovered from recycled scrap, of which a major source was spent lead acid storage batteries [20].

The recycled batteries consist of the starting-lighting-ignition type used in automotive applications as well as the industrial-type used in numerous applications, such as airport ground-support equipment, human and materials transport vehicles, industrial forklifts, load-leveling equipment for commercial electrical power systems, mining vehicles, and uninterruptible power-supply.

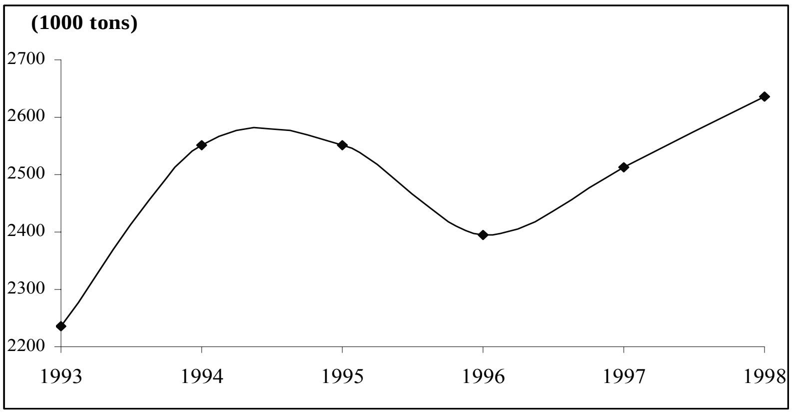


Figure 2.11 – Lead Production from Secondary Sources between 1993 and 1998

About 6% of the recycled lead was recovered from other lead-based sources, including building construction materials, cable covering, drosses and residues (new scrap) from primary smelter-refinery operations, and solder. Lead production from secondary sources between the years 1993 and 1998 is given in Figure 2.11.

### 2.5. Previous Studies on Çinkur Leach Residues

Neutral leach residues of Çinkur zinc and lead processing plant have already been an interest to both mineral engineers and metallurgists since the first production of them just after the beginning of the operations of the plant. In order to increase the zinc metal recovery and to obtain a lead-rich concentrate for lead production, diverse upgrading, beneficiation and treatment methods have been studied or tried in different periods and at different institutions in either Turkey or abroad.

Unfortunately, until today no economically feasible and/or industrially applicable treatment process or physical concentration process has been developed or has been tried in large scale. Yet, some of the previous studies have proven that if a correct combination of processes were selected, it would have not been a serious problem to treat this material. Therefore, before proceeding further; it is appropriate to mention previous studies concerning Çinkur leach residues in a chronological order.

First studies on recovering the metal values of the residues were focused on the physical concentration methods, as they are readily applicable with minimum capital and operational costs. Mountain States Research and Development Co. [21] studied the flotation potential of both leach residue and ore minerals of zinc-lead oxide ores to separate zinc and lead rich phases.

Researches on different ore bodies and leach residues showed that there would be no practical way of increasing the zinc and lead concentrations by means of flotation, heavy media separation and magnetic concentration methods. As major reasons for this phenomenon, the mineralogical properties of ore samples and residue were given. Those reasons were noted as;

- smithsonite intergrown into calcite and it was in finely disseminated form so liberation even at the smallest sizes was very limited
- zinc silicates did not float with $ZnCO_3$
- both smithsonite and zinc silicates were saturated with hydrous iron oxides
- lead and zinc were present mostly as sulphates or minerals were coated with metal sulphates thus they gave no response to concentration by flotation.

SNC Services Ltd. [22] has searched for potential leach residue upgrading methods and experimented hot acid dissolution of leach residues and conversion of iron bearing material so that upgraded lead rich phase could be further processed. Potentials and applicabilities of dissolution and three different iron precipitation methods, namely jarosite, goethite and hematite processes, were investigated for leach residue concentration. Among these potential application methods, the jarosite precipitation was proposed as the best candidate.

In another study done by Doğan Z. et.al [23], Çinkur leach residue was subjected to physical concentration methods slightly different from those of Mountain States R&D Co. The survey started with mineralogical analyses to determine the phases present, which were defined by XRD. Nevertheless, in determination of phases, due to overlapping of peaks of $PbSO_4$ on those of other phases fractional separation of phases became necessary. To get a detailed analysis of the constituents, the leach residue was deliberately dissolved in various solvents like, hot water, and ammonium acetate.

Chosen reagents dissolved $PbSO_4$, $CaSO_4.2H_2O$, and $CaSO_4.0.5H_2O$ selectively while leaving $SiO_2$ unaffected. Having defined the major compounds, gravity concentration method (slime table) was applied to increase Pb content of the leach residue.

For this purpose, a slime table was employed from which a concentrate of 27.21 % Pb content was obtained with 47.0 % lead recovery from a leach residue containing 12.19% Zn and 21.21% Pb. However, this metal concentration was still insufficient for further treatment at Çinkur in the available short rotary kiln furnace which required at least 40 % Pb in the charge. Apart from shaking table, the leach residue was processed by 3 hydrocyclones in series for concentration. This method yielded a lead concentrate as hydrocyclone overflow having 30.43 % Pb with 36.0% lead recovery.

Flotation tests were also considered as a way of increasing the lead in the final residue. However, neutralizing the pulp by CaO, sulphidizing by $Na_2S$, depressing with sodium silicate and activating with copper sulphate and finally flotation of Pb with xanthate, pine oil, etc., did not yield a lead concentrate having greater than 25.3 % Pb. For this reason, further studies concentrated on hydrometallurgical treatment methods, which proved that super hot acid leaching of residues would increase final residue's Pb content up to 31.12 % by dissolution of zinc and iron.

As an alternative treatment, Kahraman F. et.al [24] investigated sulphuric acid leaching prior to ferric chloride dissolution of leach residues. In this study, residues were first subjected to concentrated $H_2SO_4$ solution of 500 g/l $H_2SO_4$ with 1/10 solid to liquid ratio at the optimized temperature of 60°C for 4 hours which gave a zinc recovery of 45 %.

The resultant secondary leach residue (SLR) was then treated with $FeCl_3$, NaCl and HCl complex solution to dissolve Pb and recover it as $PbCl_2$. The optimum conditions for ferric chloride leaching were found to be 200 g/l NaCl, 10 g/l HCl, 160 g/l $FeCl_3$ at 100°C in 2 hours with 1/10 solid-liquid ratio. Under these optimum conditions, the recovery of lead was found to be 88 %.

Later on, a detailed investigation on utilization of these residues completed by the researchers of Istanbul Technical University [25], showed that leach residues were composed of $ZnSO_4$, $PbSO_4$, $CaSO_4.2H_2O$, $ZnO.Fe_2O_3$, $2ZnO.SiO_2$, $2FeO.SiO_2$, $Fe_3O_4$ and complex metal oxides, silicates or ferrites that were rather difficult to detect as identified phases mostly overlapped other minor compounds. In this study mainly hydrometallurgical extraction methods followed by beneficiation with flotation were applied to Çinkur leach residue containing 14.73 % Zn, 12.00 % Pb and 0.06 % Cd. Water and acid leaching experiments were followed by iron removal from solution by jarosite precipitation.

By water leaching practice, water-soluble components in the leach residue were found as $ZnSO_4$ and $CdSO_4$. Moreover, temperature of leaching was not an effective parameter in the water solubilities; therefore, it was claimed that a significant amount of water solubles might have been lost under atmospheric weathering conditions of the stockyard. The amount of the dissolved and lost zinc was estimated as 20 % of Zn originally present in leach residue.

On the other hand, acid leaching of residues by spent electrolyte (160 – 180 g/l $H_2SO_4$, 40 – 50 g/l Zn) at the optimum conditions of 90°C, 1/5 solid/liquid ratio, 2 hours retention time dissolved residue to an extent where the leach recoveries of important metals reached the following values Zn: 70 %, Fe: 60 % and Cd: 76 %.

Under these circumstances, due to excessive dissolution of iron, special care was taken to reduce the amount of dissolved iron by precipitation of iron as jarosite from iron bearing acidic solution by addition of NaOH and neutralizing effect of clinker.

Normally, the jarosite precipitate contained 2 – 3 % Zn (of jarosite weight) that was lost. The optimized precipitation was performed at 95°C and lasted for 90 minutes where NaOH and clinker were fed as jarosite converter and neutralizer, respectively. At the end of the proposed process, lead-containing cake could not be concentrated beyond 17 % Pb. Flotation studies in order to obtain a $PbSO_4$ concentrate from lead-containing cake or the original leach residue were not also successful.

Addemir O. [26] examined effects of sulphuric acid baking of the residues in two steps to convert insoluble oxides, silicates and ferrites into soluble metal sulphates while maintaining the conversion conditions of problem creating iron sulphate into ferric oxide that is insoluble in normal leaching circuit. It was shown by this study that in the first processing step, when the residue was baked with concentrated $H_2SO_4$ zinc, iron and cadmium were transformed into their sulphates at 250°C with 1.25 acid to residue ratio. If this acid baked residue was to be dissolved in water of 10 % pulp density, then 82.7 %, 64.4 %, 74.4 % of Zn, Cd and Fe would pass into the solution, respectively.

In the second step, pre-baked mix was fired for 4.5 hours in a muffle furnace heated to 650°C. After conversion of $Fe_2(SO_4)_3$ into $Fe_2O_3$, the resultant solid was leached in water, to which 90.8 % of Zn, 80.2 % of Cd and only 7.6 % of Fe passed. After filtration of the solution, SLR was analyzed and found to contain 27.13 % Pb, 1.55 % Zn, 13.67 % Fe and 0.025 % Cd.

Unfortunately, as can be predicted from the previous studies this procedure was also rejected owing to low Pb content of SLR and highly sophisticated conversion mechanism that could necessitate expensive and high temperature corrosion resistant vessels.

Another detailed investigation, performed by Saltoğlu S. et.al [27], claimed that 65 % of Zn in the residue could be recovered in the same hot acid leaching conditions as stated by [21].

However, it was reported that the zinc recovery values, both in neutral leaching and in residue treatment steps, would be further increased if in Waelz and densification kilns, the formation of complex insolubles (oxides, ferrites and silicates) were minimized. The secondary leach residue could not be concentrated further by means of flotation even though a previous report having been submitted by the Technical University of Berlin had claimed that a cake containing 40 % Pb could be obtained.

Furthermore, it was proposed not to precipitate iron in the form of jarosite, as it was considered an environmentally hazardous material in the European countries. In fact, in this study, acid baking of residues was also rejected, as there existed severe adaptation problems to the already available plant and high corrosion potential as mentioned before.

Most importantly, in this study to obtain lead and zinc from Çinkur leach residue, carbothermic reduction method was proposed. It was presumed that lead could be obtained in metallic form together with a slag phase and a gaseous phase containing no sulphur dioxide.

For this reason, reduction experiments by carbon in the presence of slag were performed. The proven data exhibited that $PbSO_4$ can be converted to PbO first under slightly reducing conditions at about 850 – 950°C by calcination. After calcination, the pelletized calcine was liquefied and reduced by the help of coke powder that was added to the melt at 1300°C in a submerged arc furnace. By this smelting action, a bullion containing most of the lead and silver, a gas phase containing most of the zinc and a slag could be obtained.

In addition to the above-cited treatment studies, some pyrometallurgical approaches were proposed. For example, CESL [19] suggested, interestingly, the use of, different lead smelting technologies unlike other researchers; because, hot acid leaching of residues was regarded as a impurity creating process while generating a non-saleable lead residue.

In terms of process characteristics and metallurgy, proven technology, operational flexibility, simplicity, hygiene and feasibility; Ausmelt, Kaldo, Kivcet and Outokumpu Flash Smelting technologies were compared to reach an economic method for the treatment of residues. As a result of this review, Kaldo process of Boliden Contech, Sweden was proposed amongst the mentioned smelting technologies.

Açma E. et.al [28] also examined the pyrometallurgical methods including, dissociation, reduction, evaporation and metallic reduction. The leach residue containing 13.15 % Pb and 15.03 % Zn was first subjected to dissociation at 850°C for 4 hours to convert zinc sulphate into zinc oxide, which was then reduced to metallic zinc and evaporated by 10 % coke powder addition at 1100°C for 2 hours.

Product compositions of the two steps were 15.40 % Pb, 18.17 % Zn for the dissociation product and 19.03 % Pb, 4.32 % Zn for that of reduction/evaporation stage.

From these results, it was found that 76 % of Zn and 14 % of Pb were reduced and vaporized. The remaining solid was further treated by metallic reduction as iron has higher affinity for sulphur than lead according to the reaction (6):

$$PbS + Fe^{\circ} \rightarrow Pb^{\circ} + FeS \qquad (6)$$

This method was chosen because most of the Pb was converted during dissociation to stable PbS that is hard to reduce by carbon. In this study, the main problem encountered was high slag viscosity. It had an increasing trend with increasing Zn % in the charge and was reduced by the addition of $Na_2CO_3$ to the charge along with Fe.

Although attempts were made to increase the metallic yield due to dissolution of PbS in the matte and slag phases, the lead recoveries were limited to below 80 %. Yet, the final products were a lead bullion of 99.6 % Pb and 0.094 % Ag with 79.2 % and 99.0 % recoveries, respectively, a zinc oxide dust with 40.62 % Zn, 4.44 % Pb and 0.12 % Cd with 85.0 %, 11.1 % and 95.0 % recoveries, respectively and a slag with a composition of 4.07 % Zn and 1.32 % Pb.

Turan M.D. et. al [35] claimed significant amounts of zinc and lead recovery from Çinkur leach residue by a two-stage recovery process which involved roasting with sulphuric acid followed by a water leaching and sodium chloride leaching of the secondary leach residue. Metallic zinc production at the first-stage from the pregnant leach solution seemed possible after proper purification and concentration. The optimum conditions for the first stage were found to be, $H_2SO_4$/Leach Residue weight ratio = 1, roasting temperature = 200°C, roasting time = 30 min, leaching temperature = 25°C, leaching time = 60 min. and pulp density = 200 g/l for 85 % zinc recovery and 50 % iron dissolution.

By the second stage brine leaching treatment, lead could be recovered, by means of $Na_2S$ precipitation, as a rich lead sulphide concentrate suitable for pyrometallurgical treatment. The optimized conditions for brine leaching were 25°C for 10 minutes leaching duration in 200 g/l NaCl solution with 20 g/l pulp density. At the optimum conditions 90 % lead recovery could be achieved.

## 2.6. Previous Studies on Other Leach Residues

In the world as mentioned above, the current processing methods are mostly in favor of sulphide ores; therefore, their resulting residues are quite different from the leach residues of the present study. In fact, most of the studies have dealt with Zn and Pb recoveries in a sequential manner; therefore, it becomes necessary to evaluate those within the same section.

First studies to increase the Zn and Pb recoveries could go back to the Second World War days. However, the changes in metallurgical processing techniques also changed the characteristics of the residues. But until today most of the studies were on hydrometallurgical wastes, namely leach residues, as they are much larger in amounts and can vary in terms of composition and physical characteristics.

The differences and problems in zinc recovery processes from leach residues have been extensively cited by Bhat K.L. and Natarajan K.A. [30]. They stated that for sulphide ores, during roasting, zinc ferrite ($ZnO.Fe_2O_3$) formation takes place, which accounts for the major loss of zinc in the hydrometallurgical treatment.

As potential remedies, rearrangement of roasting conditions, modification of the extraction circuits and development of alternative processes were proposed. Therefore, to prevent considerable amount of zinc losses, the minimization of zinc ferrite formation was suggested, this can be achieved if appropriate actions were taken.

In another research, Nii K. and Hisamatsu Y. [16] investigated the zinc ferrite formation mechanism and found that zinc ferrite formed at higher temperature (1200°C) than that formed at commonly practiced temperature (900°C) can be readily dissolved in sulphuric acid.

What they found, apart from above, were as follows:

- ores containing higher iron amounts in the form of FeS
- prolonged roasting periods
- steep increase in roasting temperature to 900°C
- solid-solid reactions between complex zinc and iron compounds

would directly hinder leaching success of the calcine and must be controlled closely.

Nonetheless, since zinc ferrite formation could not be avoided completely to recover the entrapped zinc, and mostly, its companion lead, extensive studies were done and results have been applied to operations on leach residues.

Most important advances on residue treatments were the development of Jarosite, Goethite and Hematite processes. All of these retreatment attempts were started by dissolution of leach residue in hot acid leaching conditions and further proceeded by solution purification against problem causing iron which is precipitated and filtered out in the form of jarosite, goethite or hematite whose names were accordingly given to the processes.

In Jarosite process, the residue is first subjected to hot acid leaching (HAL) where soluble Zn and Fe pass to solution to which $Na^+$, $K^+$ or $NH_4^+$ containing compounds are intentionally added to precipitate iron as jarosite according to reaction (8):

$$3Fe_2(SO_4)_3 + Na_2SO_4 + 12H_2O \rightarrow 2NaFe_3(SO_4)_2(OH)_6 + 6H_2SO_4 \quad (7)$$

The residue remained after HAL is shipped for lead production; however, the most important problem in jarosite process is due to the use of calcine as neutralizer that causes considerable zinc losses during filtration, Arregui V. et.al and Haigh C.J. et. al [31,32].

Within the past decade, in European countries Jarosite process has been classified as an environmentally hazardous method as it creates a final residue larger in amount than the unprocessed leach residue.

In Goethite process, developed by Vieille Montagne, Belgium, Gordon A.R. and Pickering R.W. [33], on the other hand, the residue is treated with unroasted ZnS to reduce ferric iron to the ferrous state according to reaction (8).

$$Fe_2(SO_4)_3 + ZnS \rightarrow 2FeSO_4 + ZnSO_4 + S^{\circ} \quad (8)$$

When complete conversion of iron is achieved, excess sulphide and elemental sulphur are separated and sent to roaster. In order to attain iron hydrolysis medium must not be acidic; so before precipitation of iron as FeOOH, solution is neutralized in pre-neutralization step.

After filtering, solution is treated with blown oxygen, to oxidize ferrous iron to the ferric state again and FeOOH crystallizes, and calcine is added, to keep acidity constant as precipitation reaction produces acid as seen in reaction (9):

$$2FeSO_4 + \tfrac{1}{2} O_{2(g)} + 3H_2O \rightarrow 2FeOOH + 2H_2SO_4 \quad (9)$$

Hematite process deals with residues in two steps, in the first one, pressure leaching of zinc leach residue takes place with a mixture of spent electrolyte, make-up acid and $SO_2$ gas at 95°C and 2 atm for three hours as Tsunoda et.al [34] reported. During this period, harmful impurities are eliminated. In the latter stage, at much higher temperatures and pressures (200°C and 20 atm), in autoclaves, ferrous to ferric iron transformation continues although reaction produces acid in high temperature and pressure hematite precipitation is not affected. The foremost limiting drawback of the process is its complexity and requirement for high cost equipment.

Attempts of Sahoo, P.K. et.al [35], for sulphatizing roasting of residues by $Na_2SO_4$, $FeSO_4$ and $H_2SO_4$ have proven the conversion of ferrous iron to ferric iron at 700°C. In addition, when the roasted residue is dissolved in water, 94 % zinc recovery without iron dissolution was reported.

Apart from sulphuric acid dissolution or sulphatizing/hot water leaching, different techniques were experimented by using various reactants. For example, by Beckstead [36], chlorination of residues was investigated by brine leaching process that used HCl, $CaCl_2$ and $Cl_{2(g)}$ which reacted with zinc oxide or ferrite to give water soluble zinc chloride as given below. This development was applied to leach residues, to meet environmental protection regulations against toxic wastes:

$$ZnO.Fe_2O_3 + 2HCl \rightarrow ZnCl_2 + Fe_2O_3 + H_2O \qquad (10)$$

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \qquad (11)$$

Bhat et.al [37] surveyed, on the contrary, the potential of cathodic electroleaching and reported complete recovery of zinc and iron at room temperature. It was claimed that both reductive dissolution and creation of anion vacancies were responsible for the dissolution of zinc ferrite in the leach residue.

Iron was removed from the system by oxidation of ferrous ions to ferric ion and precipitation of iron by regulating acidity of the solution. The effective parameters were found to be current density, electrolyte concentration, time and pulp density.

In the caustic soda leach process of Eacott et. al [38], zinc and lead were selectively dissolved in sodium hydroxide rejecting iron in the residue. The leach solution after purification with zinc dust was electrolyzed to produce metal regenerating sodium hydroxide according to the reactions:

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O \qquad (12)$$

$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O \qquad (13)$$

$$2Na_2ZnO_2 + 2H_2O \rightarrow 2Zn + 4NaOH + O_2 \qquad (14)$$

The process has been used for the dissolution of zinc from different oxidized ores and secondary materials. Furthermore, in this study a techno-economic feasibility study of the caustic leach-electrowinning process was made and claimed that it could be applied to small, medium or large-scale operations, relatively clean in terms of work place and ambient air emissions. Solid-liquid separation was however, somewhat difficult with concentrated caustic solutions and very fine solids, yet the separation could be achieved with conventional equipment.

In another process for electric arc furnace dust (EAFD) treatment, Wheatley B.I. and Pooley F.D [39], used high intensity magnetic field to settle the slurry after caustic leach and then filtered in a filter press. Leach recoveries of 80 % zinc and 90% lead have been reported. Unrecoverable zinc was mainly present as ferrite, which could be recovered by the reduction roasting of the EAFD before leaching, but in this case, the lead recovery could become low, as lead oxide was reduced to metallic lead.

Another method developed by Roeder A. et.al. [40], for complete utilization of leach residues, were that in which the leach residue was mixed with large quantity of pyrite cinders by adding NaCl. Then, the mixture was subjected to chloridizing roasting in multiple hearth furnaces. The elements Zn, Cu, Cd, Ag and Au were rendered soluble and were separated from the iron oxide by percolation leaching.

In addition to these processes, Youcai, Z. et.al. [41] investigated NaOH treatment methods for $ZnCO_3$ ores for direct dissolution of zinc in concentrated alkaline solution. It was shown that the leaching of lead could be improved remarkably with the addition of NaCl to the leaching system.

EZINEX process developed by Engitec Impiant in Italy to treat 500 tons per year EAFD to produce cathode zinc employed ammonium chloride-sodium chloride lixiviant for the dissolution of zinc at 70–80°C for 1 h. The main leaching reaction was written by Olper et. al. [42] as:

$$ZnO + 2NH_4Cl \rightarrow Zn(NH_3)_2Cl_2 + H_2O \qquad (15)$$

Other metals present in the dust, i.e. copper, cadmium, nickel, lead and silver reacted with the same mechanism. The iron oxides, ferrite and silica were not dissolved during this step. The leach solution was purified by zinc cementation process. Zinc metal was produced from the purified zinc amino chloride electrolyte by electrolysis in an open cell without evolution of chlorine at the anode.

In Belgium, C.S. Ek [43] tried ammonium sulfate and Diethylene Triamine (EDTA) leaching methods. In these trials, $NH_4(SO_4)_2$ gave partial conversion of insoluble $PbSO_4$ to soluble PbS. But EDTA totally complexed $PbSO_4$ and after $CO_2$ gas purging, the solution converted to $PbCO_3$. But, in this process while stripping Pb from solution by the addition of EDTA, some entrapped solvent and Pb increased the toxicity of the waste further, therefore, the solution had to be purified that could cause an extra expense.

Generally leach residues are deficient in sulphur and their conversion by roasting, hot acid leaching and by other processes are not yielding acid or water soluble compounds. So, some sulfide bearing additives are used along with alkaline.

In the light of this assumption, a process employing sequential treatment by NaCl and/or $Na_2S$ of secondary leach residue was found promising for Pb recovery in the saleable form of PbS.

In this research, Raghavan R. et.al [44] tried to define the optimum parameters for conversion of $PbSO_4$ to PbS by hydrometallurgical methods. Thus, two different routes were found to obtain PbS. Reactions of these routes were:

$$PbSO_4 + Na_2S \rightarrow PbS + Na_2SO_4 \qquad (16)$$

$$PbSO_4 + 2NaCl \rightarrow PbCl_2 + Na_2SO_4 \qquad (17)$$

$$PbCl_2 + Na_2S \rightarrow PbS + 2NaCl \qquad (18)$$

The optimum conditions for brine leaching and PbS precipitation were found to be 20 g/l pulp density, 300 g/l NaCl concentration, 15 minutes reaction time and 30°C solution temperature. Under these conditions, it was reported that total recovery of Pb was possible.

Apart from residues of primary zinc or lead production methods, processes were also developed for spent lead acid battery recycling in order to recover lead. Among the processes, PLINT Process is the most promising, by this method closed-loop hot brine leaching process is basically applied to the spent battery scrap in four basic steps, i.e. leaching, iron and sulphur removal, precious metal recovery and lead recovery. The process yields a lead containing complex intermediate product of $Na_2PbCl_4$, which is further treated by calcium hydroxide or sodium carbonate to precipitate lead as lead hydroxide or carbonate according to following reactions [45].

$$PbSO_4 + 4NaCl \rightarrow Na_2PbCl_4 + Na_2SO_4 \qquad (19)$$

$$Na_2PbCl_4 + Ca(OH)_2 \rightarrow Pb(OH)_2 + CaCl_2 + 2NaCl \qquad (20)$$

$$Na_2PbCl_4 + Na_2CO_3 \rightarrow PbCO_3 + 4NaCl \qquad (21)$$

# CHAPTER 3

# SAMPLE CHARACTERIZATION,
EXPERIMENTAL SET-UP and PROCEDURE

In this section, the physical, chemical and mineralogical characteristics of the leach residues and their determination methods are given first. Afterwards, the experimental set-up employed in leaching experiments of Çinkur leach residues is explained in detail together with experimental procedure.

## 3.1. Brief Description of Çinkur and Neutral Leach Residues

Çinkur is the only electrolytic zinc production plant of Turkey having an annual zinc production capacity of 40,000 tons. In a period of about 20 years, starting from its establishment in 1976, carbonate type ores mined in Turkey have been used as the main raw material.

After its privatization in 1997, the plant has only processed a concentrate (calcine) imported from Iran by direct leaching for 3 years. In the year 2000, the plant was shut down due to low efficiency, high-energy expenses and decreased zinc prices in the world. A simplified flowsheet of Çinkur plant can be seen in Figure 3.1.

For this research, the neutral leach residues of Çinkur, considering both origins, were obtained from plant waste disposal area that has been weathered for years. Total amount of leach residues is approximately 1,200,000 tons, a major constituent of which has been produced from Turkish ores and the remaining minor portion was processed from Iranian concentrate.

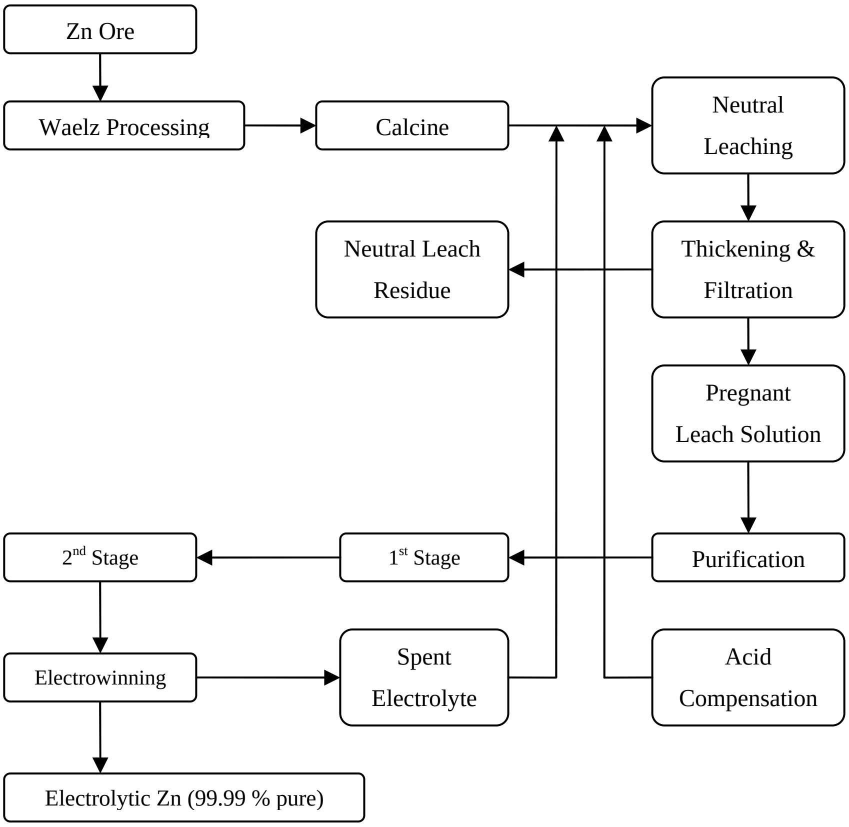


Figure 3.1 – Flowsheet of Waelz – Leach – Electrowinning System at Çinkur

## 3.2. Obtaining Leach Residue Samples from Waste Disposal Area

The samples of two different kinds of leach residue were taken from Çinkur waste disposal area on October 6th, 2003. The Turkish leach residue sample was 12 kg while the weight of Iranian leach residue was 14 kg and the samples were taken from the surfaces of each stock pile and in depth sampling was not possible.

Çinkur plant has not been in operation since the year 2000, so reaching exact figures related to plants' waste amount was not possible. However, some limited information on approximate amounts of different types of leach residues was obtained from the retired operation engineers.

Based on the information obtained, the samples of the leach residues of Turkish and Iranian origin were mixed in a ratio of 9 to 1 after drying at 105ºC and grinding by the use of a pulverizer.

According to official statistics, the annual residue production was around 25,000 tons; however, due to absence of the optimum operational conditions, far more amounts of residues had been produced in years and today existing total amount is estimated to be around 1.2 million tons in two different characteristics.

Owing to previous knowledge on waste properties, the samples were taken from the leach residue of Turkish ores and leach residue of Iranian concentrate, deliberately. These two sources were different in characteristics since they have exhibited different behavior under atmospheric conditions. Turkish origined leach residue was relatively dry, brittle and older as compared to Iranian origined leach residue that was rather wet, plastically formable and more recently produced.

Figure 3.2 – View of Çinkur Waste Stockyard

Waste disposal area at Çinkur, however, was and it still is in uncontrolled condition where Waelz kiln slag, leach residues and 1st and 2nd purification cakes have been stock piled in very close vicinity and prone to mixing in each other. A photographic view on Çinkur waste stockyard is given in Figure 3.2.

## 3.3. Characterization of Leach Residues

Leach residues obtained from the two different sources have been characterized within the scope of this thesis. The characterization of Turkish and Iranian leach residues included the physical, chemical and mineralogical investigations of the taken samples.

### 3.3.1 Physical Characterization

Amount of physically present water is very important in all material processing considerations as energy, transportation and processing expenses depend on the moisture content of raw materials.

As a result, as the first step of determination of the properties, moisture contents of the two leach residues were found. For this purpose, 5,000 grams representative portions of leach residues were weighed and heated to 105°C in a drying oven. After reaching constant weight and cooling to room temperature, samples were re-weighed. As a result, the moisture contents of Turkish and Iranian leach residues were found as 19.5 % and 30.9 %, respectively.

Later, density determinations were carried out, as density is one of the key factors in handling and storage of raw materials, residues and products. Therefore, as the second step in physical property determination, the bulk density and specific gravity of pulverized sample were investigated.

For bulk density determination, a 1-l measuring cylinder was used and bulk density value of the composite sample, which was a blend of 9 units of Turkish and 1 unit of Iranian leach residues, was found to be 0.79 g/cm$^3$.

Furthermore, specific gravity determinations were performed by using air and water pycnometers. These two techniques gave the following results for the same blend as 3.93 and 4.38, respectively. The difference between the two measured values was considered to be due to the presence of water soluble zinc and cadmium sulphates in the sample.

For similar reasons cited above, the particle size of materials is quite important and as a part of physical properties, it must be analyzed in detail. As a normal procedure, 150 grams of pulverized blend of leach residues was wet screened on a nest of 6 screens varying in aperture sizes which had a range from 315 μm to 38 μm in order to obtain particle size distribution.

Major particle size fraction of the wet sieved sample was found to be below 38 μm. Similarly, the existence of water soluble phases, as stated above, resulted in 5.89 % weight loss in wet screen analysis.

Table 3.1 – Wet Screen Analysis of Blended Leach Residues

| Microns | Percentage (%) | Cumulative Oversize (%) | Cumulative Undersize (%) |
|---|---|---|---|
| **315** | 23.12 | 23.12 | 76.88 |
| **100** | 8.95 | 32.07 | 67.93 |
| **75** | 5.60 | 37.67 | 62.33 |
| **53** | 5.87 | 43.54 | 56.46 |
| **45** | 1.76 | 45.30 | 54.70 |
| **38** | 1.68 | 46.98 | 53.02 |
| **Pan** | 47.13 | - | - |
| **Total** | **94.11** | **5.89 % Dissolution in Water** | |

### 3.3.2. Chemical Characterization

The samples of leach residues obtained from the plant stockyard were analysed by Perkin – Elmer model 2380 Atomic Absorption Spectrophotometer (AAS) after grinding the representative samples taken to a very fine size and dissolution in aqua regia with HF addition in Teflon® beakers.

Precautions were taken so as to completely dissolve the samples excluding unreacted carbon and to avoid precipitation. The results of chemical analyses obtained at the chemical analysis laboratories of the Department of Metallurgical and Materials Engineering of METU were compared with those of previous researchers and the results were found to be meaningful with reasonable deviations.

Table 3.2 – Chemical Compositions of Turkish, Iranian and Blended Leach Residues

| | **% Zn** | **% Pb** | **% Fe** | **% Cd** |
|---|---|---|---|---|
| **Turkish LR** | 12.26 | 15.75 | 6.36 | 0.054 |
| **Iranian LR** | 15.57 | 6.98 | 7.30 | 0.049 |
| **Blended Leach Residue** | 12.59 | 15.21 | 6.45 | 0.054 |

### 3.3.3. Mineralogical Characterization

During the screen analyses of blended leach residues, some magnetic particles were observed in coarse fractions. To define the origin of these particles low intensity magnetic separation tests were performed on leach residues at 5,000 Gauss by using Davis Tube at the mineral dressing laboratory of the Department of Mining Engineering of METU. The small amounts of magnetic fraction were separated and these were subjected to Satmagan measurement at the chemical analysis laboratories of the Department of Metallurgical and Materials Engineering of METU.

These separation tests indicated that the separated magnetic portion of Turkish leach residue and that of Iranian leach residue were composed of magnetite and other magnetic compounds. Then, the X-ray diffractograms (XRD) of the two leach residues were taken as seen in Figures 3.3 and 3.4 by using 100 kV Philips twin tube X-ray diffractometer (PW/1050) at the Department of Metallurgical and Materials Engineering of METU.

Detailed analyses of XRD patterns indicated the presence of $PbSO_4$, $CaSO_4.2H_2O$, $CaSO_4.0.5H_2O$, $ZnO.Fe_2O_3$, $ZnSO_4.7H_2O$, $Fe_3O_4$ and $2FeO.SiO_2$ as major phases. However, some of the peaks and their corresponding components could not be defined because of the complex nature of the leach residues.

Finally, as scanning electron microscopy (SEM) is able to give point and line analyses of undefined constituents of samples, the leach residues were analyzed by SEM for which JEOL JMS 6400 type scanning electron microscope equipped with EDS Tracor Series II analysis system was used after coating the samples with gold.

During SEM analyses while point analyses were taken to define major phases, line and area analyses were done to obtain an outline of the existing elements present in both residues as see in Figures 3.5 and 3.6.

In fact, based on the analyses of SEM, it was concluded that the phases, which were determined by the use of XRD, were found to be consistent with SEM results. Furthermore, it was considered that undefined peaks of the XRD diffractograms might be Mg and Al containing oxides or complex silicates that were present in smaller amounts and were rather difficult to determine, especially when there were major peaks of overlapping phases, such as $PbSO_4$ and $CaSO_4.2H_2O$.

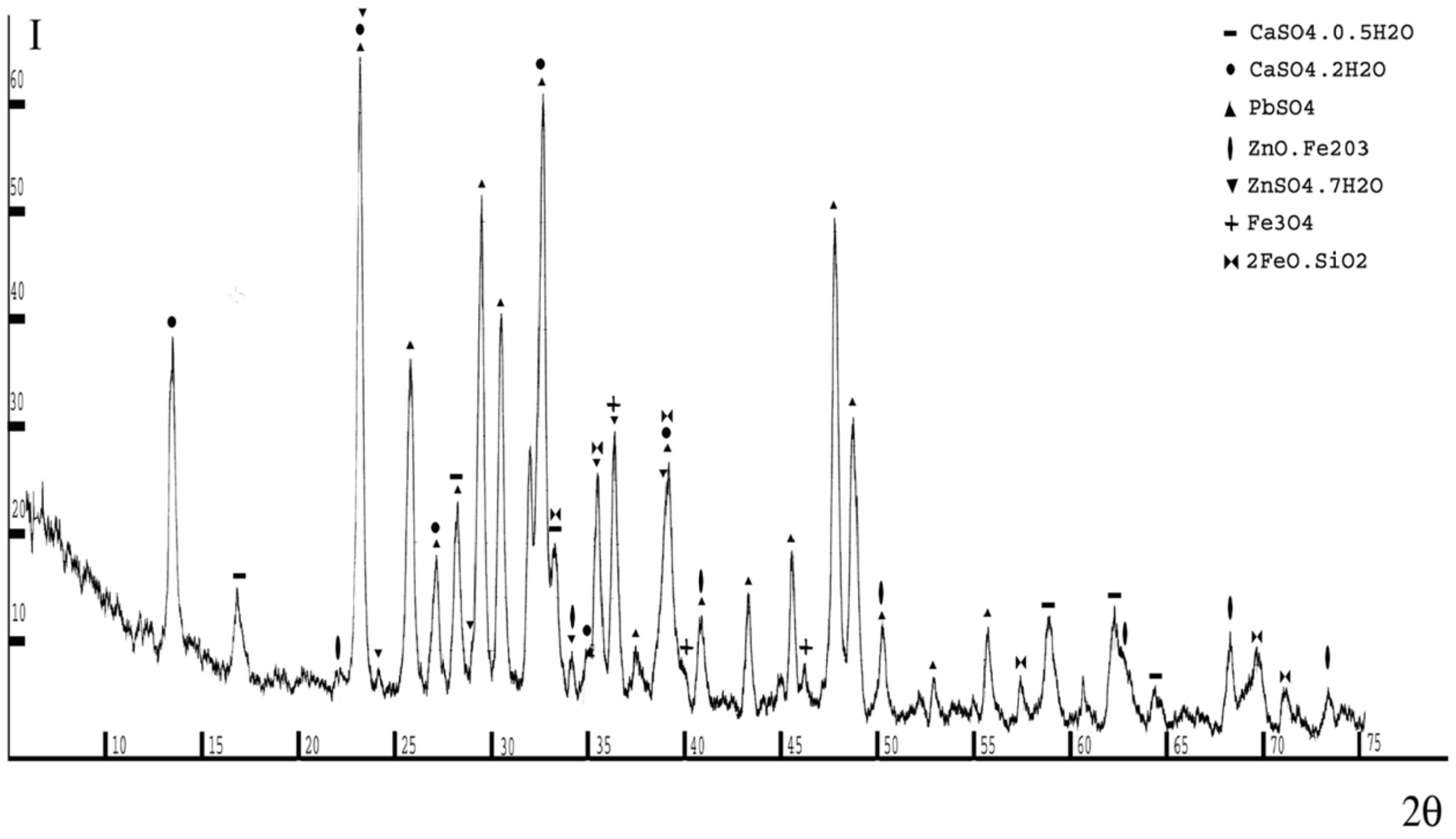


Figure 3.3 – XRD Pattern of Turkish Leach Residue

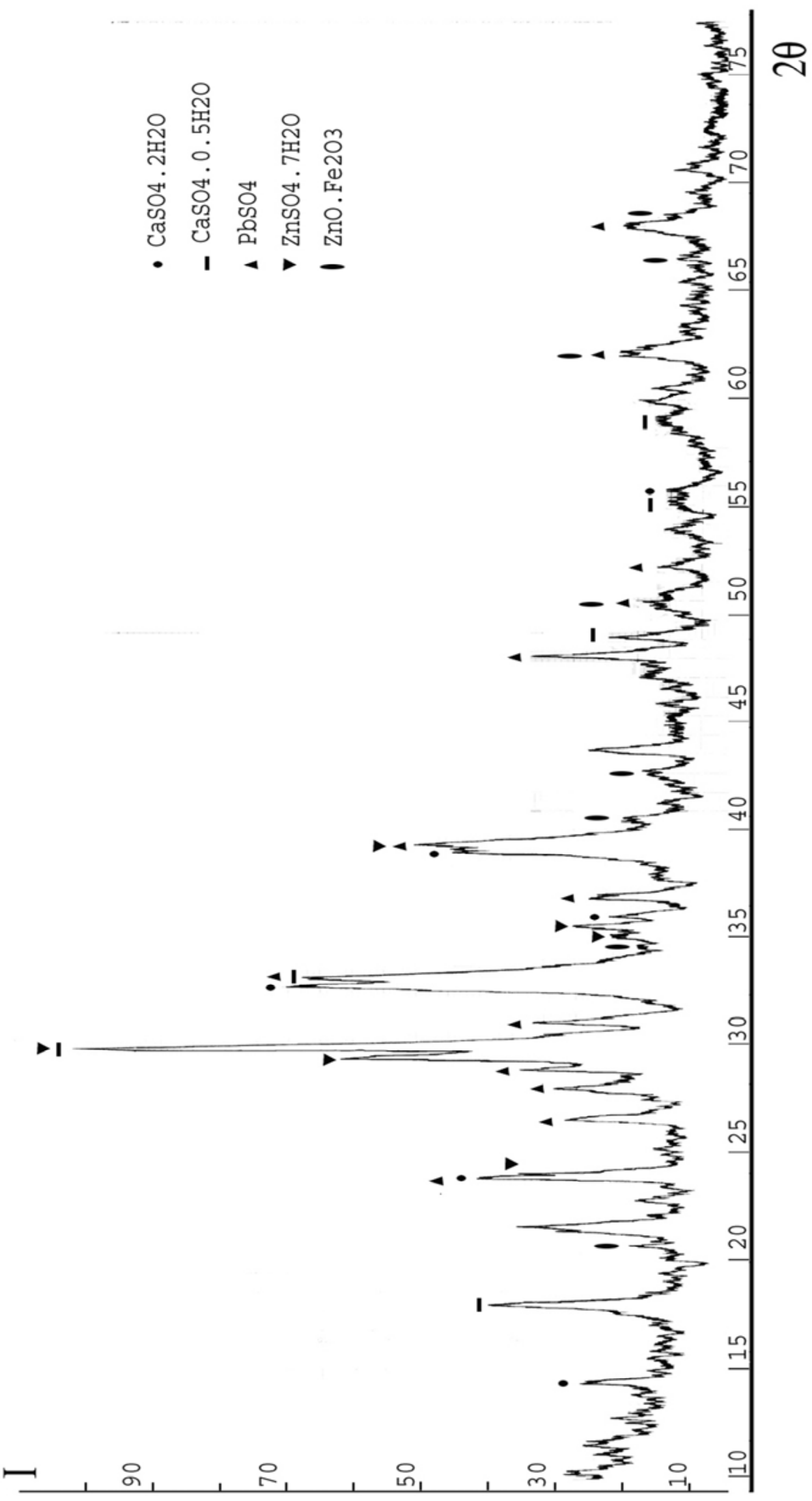


Figure 3.4 – XRD Pattern of Iranian Leach Residue

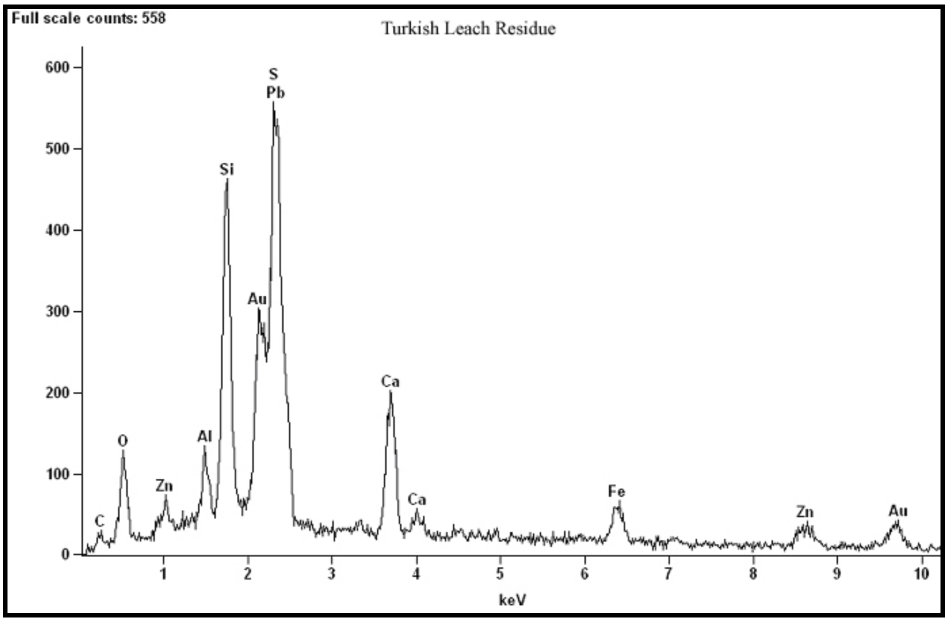


Figure 3.5 – XRD Pattern of Turkish Leach Residues (taken from EDS Tracor Series II System)

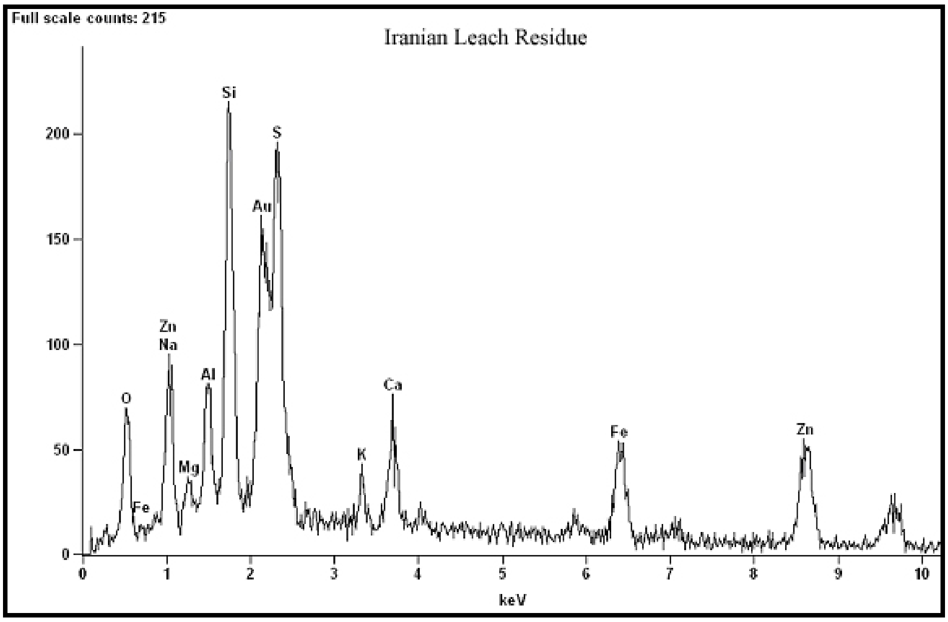


Figure 3.6 – XRD Pattern of Iranian Leach Residues (taken from EDS Tracor Series II System)

## 3.4. Experimental Set-up and Procedure

Having defined the physical, chemical and mineralogical properties of the leach residues; water, acid and brine leaching tests were considered for zinc and lead recovery from the blended leach residues.

During the leaching experiments Velp Scientifica AREX2 model hot plate with Teflon coated magnetic stirrer and 250 ml Pyrex balloons with three necks were used at constant temperature that was adjusted by a contact thermometer having ± 2°C sensitivity. Also a water cooled Liebig condenser was attached to the system to avoid most of the evaporation losses at high temperatures. The magnetic stirrer speed was kept constant in all of the experiments in order to obtain sufficient mixing of solid and liquid. A schematic drawing of the set-up can be seen in Figure 3.7.

The procedure followed for the recovery of zinc and lead was started with water leaching experiments defining first the variables as temperature, time and particle size and the constants as pulp density and stirring speed. In each experiment one of the variables was changed while keeping constant the others.

In water leaching experiments, deionized water of 100 ml volume was heated to a predefined temperature and at the desired temperature 25 grams of pulverized blend was added. At the instant of addition, the duration for leaching was started to be counted. After dissolution of water solubles from the blend, pulp was filtered, insoluble solids washed, dried and weighed. The resultant filtrate was then analyzed by AAS for its zinc content. Finally, the recovery of zinc by water leaching was calculated.

As the major candidate for zinc recovery from the blended leach residues, hot sulphuric acid leaching tests were performed by considering the variables as acid concentration, time, temperature, and particle size. The sulphuric acid used was Merck quality which was 95 – 98 % $H_2SO_4$ by volume.

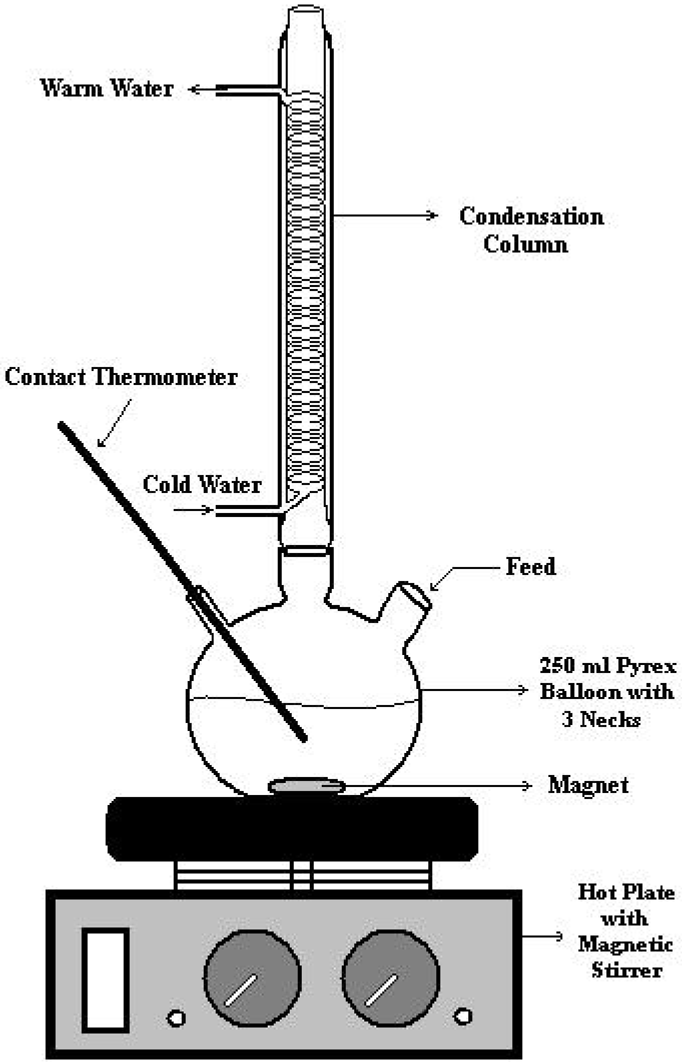


Figure 3.7 – Schematic View of the Experimental Set-up

The acidities of the final leach solutions were measured at a precision of ± 0.1, at room temperature by using Mettler – Toledo pH meter. A similar procedure to the one described for water leaching was used in hot acid leaching. After leaching, the pregnant leach solution was separated by filtration and the leach residue was washed with distilled water, dried and weighed.

The leach residues were analyzed by AAS for their Zn, Pb, Fe and Cd contents. Occasionally, the pregnant leach solutions where chemically checked for mass balance calculations. So, the optimum conditions for acid leaching were determined after a series of leaching tests.

After the determination of the optimum conditions for zinc dissolution by hot acid leaching, brine leaching tests were applied to a stock of secondary leach residue obtained from the hot sulphuric acid leaching experiments.

In these experiments, Merck quality 99.5 % extra-pure solid NaCl was dissolved in distilled water such that the resultant solution can be used as the lixiviant. A similar leaching procedure to that has been used in acid leaching was applied in brine leaching experiments. The major variables investigated were NaCl concentration, and pulp density. A few experiments were also carried out at different leaching durations, temperatures and particle sizes. The final leach residues were analyzed for their lead metal contents by AAS after each experiment. Finally, the leach residues of water, hot acid and brine leaching obtained under the determined optimum conditions were analyzed by XRD.

# CHAPTER 4

# RESULTS and DISCUSSION

As the aim of this study, zinc and lead recovery potentials from Çinkur neutral leach residues were investigated by using hydrometallurgical methods. In other words, the leaching of zinc and lead were taken as the main concern, together with iron dissolutions and cadmium recoveries under various conditions in aqueous solutions, namely water, sulphuric acid and brine solutions. Before starting the leaching experiments, the blended leach residues of Çinkur has undergone a detailed physical, chemical and mineralogical characterization to determine the phases present and to find out their potential solvents. The results of characterization and the interpretation of data were explicitly given in Chapter 3; thus, there would be no need to recite them in this section.

In this chapter, the results of different experimental procedures are going to be presented and discussed in detail, in terms of process parameters, which were chosen in general as reaction time or duration, temperature, reactant concentration, pulp density and particle size of the feed.

## 4.1. Water Leaching Studies

Since water is the most abundantly available and the cheapest solvent, the initial experiments were done with water. In water leaching trials temperature, retention time and particle size of the blend of leach residues were selected as the parameters to be investigated.

Water leaching tests were done by using the experimental set-up explained in Section 3.4, at a constant volume of 100 ml of de-ionized water that was heated to a predefined temperature at which 25 g of feed (pulverized blend of leach residues) was added. The pregnant solutions obtained after filtration were then diluted with de-ionized water up to a volume of 3 liters to avoid interference and were analyzed by AAS for their zinc contents.

Zinc recoveries as weight percent were calculated by using the following formula when the analyses were completed on leach liquors:

$$\%\Re = \frac{Zn_{Solution} * V_{Solution}}{Zn_{LR} * W_{LR}} * 100$$

where $Zn_{Solution}$, $Zn_{LR}$, are the analyzed zinc content of pregnant leach liquor in g/l, and the zinc content of the blended leach residues in wt %, respectively, and $V_{Solution}$ is the volume of leach liquor in liters, $W_{LR}$ is the weight of initial feed or blended leach residues.

### 4.1.1. Effect of Temperature on Zinc Recoveries

The first set of experiments on water leaching were done to determine the effect of temperature on water solubility of blended leach residues and thus to determine the percent recovery of zinc while keeping pulp density and reaction time constant at 250 g/l and 2 h, respectively.

As can be seen from both Table 4.1 and Figure 4.1, the recovery values of zinc slightly increased when the temperature was raised from room temperature to near boiling point. However, the recoveries of zinc did not reach to industrially acceptable limits and varied in a narrow range from 7.83 % to 10.26 % at a final pH of about 5.9.

In fact, this behavior can be explained as, zinc, in the form of sulphates, or hydrated sulphates that were also detected in XRD analyses, dissolved in water.

Furthermore, such a trend seemed quite consistent with the previous studies [22 – 27], as they stated the existence of water soluble zinc sulphates up to 40 % of the entire zinc content of freshly produced leach residues most of which was washed away by rain water during storage.

Table 4.1 – Change of Recovery of Zinc with Temperature in Water Leaching

| Experiment Code | Temperature (°C) | Zinc Recovery (%) |
|---|---|---|
| WL 1 | 25 | 7.83 |
| WL 2 | 70 | 9.24 |
| WL 3 | 95 | 10.26 |
| Reaction time = 2 h, Pulp density = 250 g/l | | |

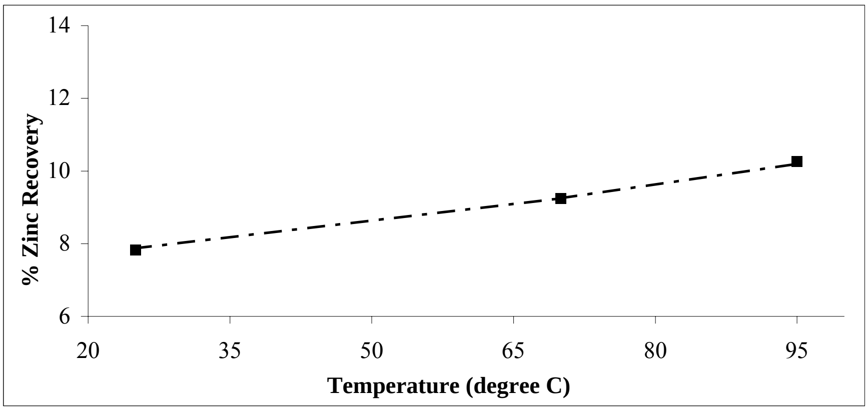


Figure 4.1 – Recovery of Zinc vs. Temperature in Water Leaching

### 4.1.2. Effect of Reaction Time on Zinc Recoveries

As the second parameter in determining the optimum conditions for water leaching, reaction times were altered under controlled conditions. For this purpose, the leaching durations were chosen as 2, 6 and 18 hours whereas pulp density and leaching temperature were kept constant as 250 g/l and 25°C.

Referring to the results given in Table 4.2 and presented in Figure 4.2, it was seen that an increase in dissolution period was found to be leading to a slight increase in recoveries of zinc.

This is because zinc was mostly present in the form of water insoluble compounds such as zinc ferrite, zinc silicate, etc. in the blended leach residues.

The zinc recoveries were limited by the amount of zinc sulphate present in the residues. Moreover, even though zinc sulphate amounts were stated to be much higher in the literature, the expected recoveries were not achieved, because zinc sulphate present in the freshly produced leach residues was washed away by rain water during their long period of storage in Çinkur stockyard.

Table 4.2 – Change of Recovery of Zinc with Reaction Time in Water Leaching

| Experiment Code | Reaction Time (h) | Zinc Recovery (%) |
|---|---|---|
| WL 1 | 2 | 7.83 |
| WL 4 | 6 | 10.20 |
| WL 5 | 18 | 12.45 |
| Temperature = 25 °C, Pulp density = 250 g/l | | |

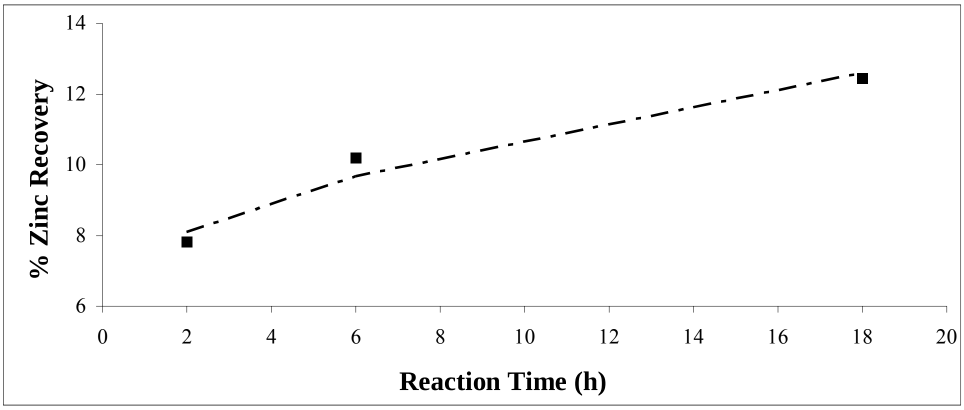


Figure 4.2 – Recovery of Zinc vs. Reaction Time in Water Leaching

Finally, the same test procedure was applied to a finer particle sized feed material which was obtained by grinding the original blended leach residues (initial particle size = 62.3 % below 75 microns) to 89.5 % below 75 microns.

Unfortunately, such liberation or increasing of specific surface area operation attempts of the blended leach residues did not raise the zinc recovery by more than 0.82 % at 25°C in 2 hours of water leaching with a pulp density of 250 g/l. Besides, XRD patterns of water leach residues were also investigated, but, the excessive overlapping of dominating phases in the residue did not allow clear interpretation of the data.

Eventually, it was concluded that a rise in temperature or dissolution period or a decrease in particle size could yield slightly higher recoveries of zinc but such small increases would not be sufficient for industrially feasible treatment by water leaching.

Yet, if an additional water leaching step were to be put into operation in an existing production line in a hydrometallurgical zinc plant, the production efficiencies would be increased by approximately 10 % by recovering zinc form stock piled leach residues. Higher recoveries of zinc from freshly produced leach residues would obviously be expected.

## 4.2. Acid Leaching Studies

Insufficient zinc recoveries of water leaching tests and XRD analyses of the blended leach residues have indicated that acidic medium will be more effective in dissolving the zinc bearing compounds, such as zinc ferrite and zinc oxide. In acid leaching experiments, sulphuric acid was chosen as the solvent as it is readily available in the market or as by-product in most of the hydrometallurgical zinc plants and is inexpensive when compared other acidic media such as nitric and hydrochloric acids.

Acid leaching experiments dealt with the optimization of the leaching parameters, which were taken as acid concentration, reaction time, temperature, and particle size.

In this part, unlike water leaching experiments, the zinc recoveries were calculated according to the given formula below, by considering the analyses of undissolved portion of the blended leach residues, or secondary leach residue.

$$\%\Re = \left(1 - \frac{Zn_{SLR} * W_{SLR}}{Zn_{LR} * W_{LR}}\right) * 100$$

where $Zn_{LR}$, $Zn_{SLR}$, are the analyzed zinc contents of primary (blended residues) and secondary leach residues in wt %, respectively, and $W_{LR}$, $W_{SLR}$ are the weights of initial feed and undissolved portion of leach residue, respectively.

### 4.2.1. Effect of Acid Concentration on Zinc Recoveries

Among the effective factors, initial sulphuric acid concentration was taken into consideration first while the reaction time, temperature and pulp densities were kept constant as 2 h, 95°C and 250 g/l, respectively. Results of the experiments can be seen in Table 4.3 and Figure 4.3.

The results simply indicated that when the acid concentration was increased from 0 to 250 g/l, zinc recoveries and iron dissolution values increased substantially. However, their trends differed considerably that the zinc leach recoveries after exceeding 100 g/l $H_2SO_4$ limit reached a plateau where it remained almost constant. On the contrary, iron dissolved more in concentrated acid solutions and followed almost a linear trend throughout the studied acid concentration range.

Such trends were already reported by other researchers, for increasing acid concentrations, dissolution periods and leaching temperatures [24 – 27]. At this point, the zinc recoveries and iron dissolutions must be considered simultaneously in terms of process metallurgy and economy. If higher zinc recoveries are desired with higher iron dissolution values, higher acid concentrations can be selected; however, the iron dissolution must be controlled very carefully, as dissolved iron reduces the zinc electrowinning efficiency.

Table 4.3 – Change of Recoveries of Zinc and Iron with $H_2SO_4$ Concentration in Acid Leaching

| Experiment Code | $H_2SO_4$ Concentration (gpl) | Zinc Recovery (%) | Iron Recovery (%) |
|---|---|---|---|
| WL 3 | 0 | 10.26 | 0.00 |
| AL 1 | 50 | 62.55 | 16.76 |
| AL 2 | 100 | 73.28 | 34.65 |
| AL 3 | 150 | 74.87 | 39.59 |
| AL 4 | 200 | 74.77 | 48.26 |
| AL 5 | 250 | 75.42 | 55.79 |
| Reaction Time = 2 h, Temperature = 95 °C, Pulp Density = 250 g/l | | | |

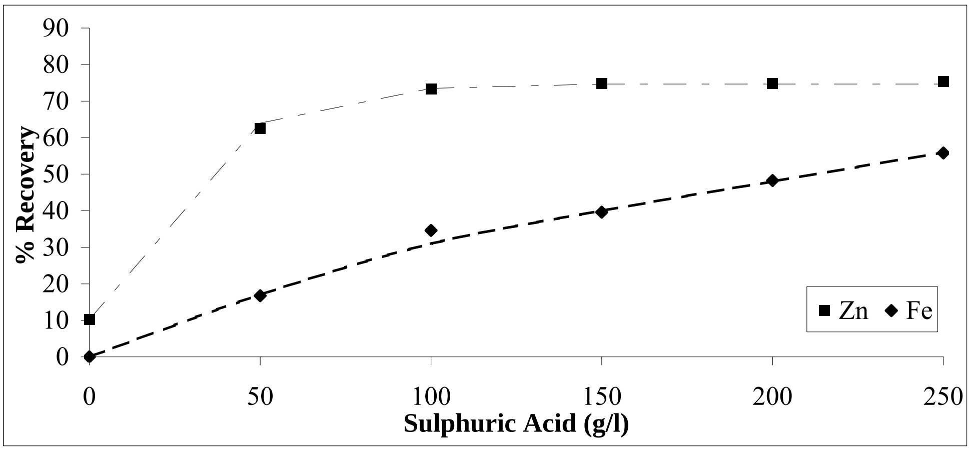


Figure 4.3 – Recovery of Zinc and Iron vs. $H_2SO_4$ Concentration in Acid Leaching

Moreover, it must be eliminated from solution by one of the previously mentioned iron removal methods, such as jarosite, goethite, and hematite processes, each of which produces a new iron-bearing residue that may be in higher amount or creates expenses that can be higher than the income coming from the increased recovery of zinc.

Consequently, when process metallurgy and economy were considered extensively, although 100 g/l $H_2SO_4$ acid concentration looked promising, it could be concluded that 150 g/l $H_2SO_4$ would be more suitable. Because the required acid would easily be supplied from spent electrolyte without any additional acid or neutralizing agent requirement and purification expenses of 5 % extra iron dissolution could be compensated by utilization of this readily available source and by the increase in zinc recovery of about 1.6 %.

### 4.2.2. Effect of Temperature on Zinc Recoveries

Having determined the optimum acid concentration as 150 g/l $H_2SO_4$ at 2 hours reaction time with 250 g/l pulp density, the leaching temperatures were varied in a range from room temperature to near boiling point temperature of 95°C, at which point the process is termed as hot acid leaching by many researchers. The results of experiments done at different temperatures can be interpreted in terms of recovery of zinc and amount of iron dissolved in the solution.

Table 4.4 – Change of Recoveries of Zinc and Iron with Temperature in Acid Leaching

| Experiment Code | Temperature (°C) | Zinc Recovery (%) | Iron Recovery (%) |
|---|---|---|---|
| AL 6 | 25 | 65.28 | 0.00 |
| AL 7 | 50 | 68.10 | 4.50 |
| AL 8 | 80 | 72.06 | 37.38 |
| AL 3 | 95 | 74.87 | 39.59 |
| $H_2SO_4$ Concentration = 150 gpl, Reaction Time = 2 h, Pulp Density = 250 g/l | | | |

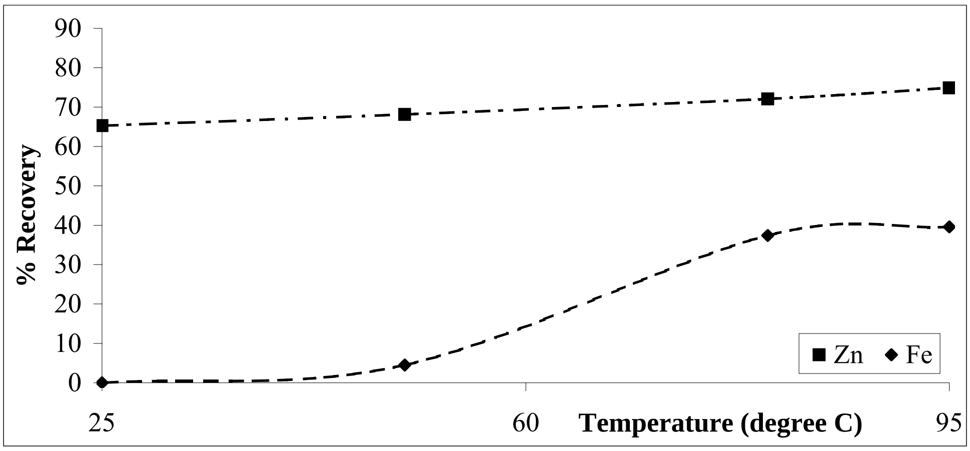


Figure 4.4 – Recoveries of Zinc and Iron vs. Temperature in Acid Leaching

As seen from the results given in Table 4.4 and Figure 4.4, the leach recovery of zinc increased with increasing temperature and reached a maximum at 95°C. However, at the same time the dissolution of iron sharply increased which was expected, as iron solubility is a function of temperature, acidity and time.

In other words, iron solubility can be kept at a minimum by manipulating the dissolution conditions or decreasing the reaction time, temperature and acid concentration. So, temperature was chosen as 95°C for the following experiments, as the zinc recovery yielded its maximum value with tolerable iron content in pregnant leach solution.

### 4.2.3. Effect of Reaction Time on Zinc Recoveries

The third set of acid-related experiments was on reaction time and its effect on recovery of zinc and dissolution of iron. For this study, the leaching duration was varied between 1 hour and 8 hours while the sulphuric acid concentration, temperature and pulp density were maintained at 150 g/l, 95 °C and 250 g/l, respectively.

Since the recoveries of the metals can be improved at prolonged periods, it was intended to find such relations for zinc and iron. Results of these experiments are given in Table 4.5 and Figure 4.5.

From the results, it could be deduced that zinc and iron leach recoveries increased substantially during the initial 2-hour period thereafter the changes were limited. There existed a small discrepancy in the leaching behavior of zinc, which could be due to the experimental errors or variations in chemical analyses.

Table 4.5 – Change of Recoveries of Zinc and Iron with Reaction Time in Acid Leaching

| Experiment Code | Reaction Time (h) | Zinc Recovery (%) | Iron Recovery (%) |
|---|---|---|---|
| AL 9 | 1 | 69.18 | 30.93 |
| AL 3 | 2 | 74.87 | 39.59 |
| AL 10 | 4 | 68.16 | 39.63 |
| AL 11 | 5 | 70.30 | 39.06 |
| AL 12 | 6.5 | 72.39 | 44.20 |
| AL 13 | 8 | 79.09 | 47.72 |
| $H_2SO_4$ Concentration = 150 gpl, Temperature = 95 °C, Pulp Density = 250 g/l | | | |

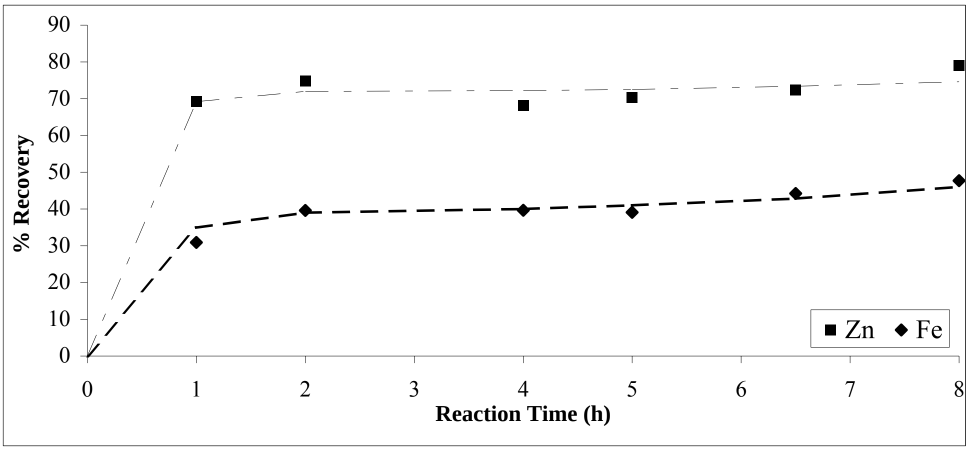


Figure 4.5 – Recoveries of Zinc and Iron vs. Reaction Time in Acid Leaching

As a conclusion of the results of acid concentration, temperature and reaction time experiments of acid leaching, it can be claimed that the optimum conditions, resulted in 74.87 % zinc recovery and 39.59 % iron dissolution, were at 150 g/l $H_2SO_4$ concentration, 95°C leaching temperature, 2 hours leaching duration at a pulp density of 250 g/l with a final pregnant solution pH of 4.2.

The optimized values were checked for their reproducibility by repeating the same experiment 3 times and the results obtained were found to be reproducible and within an acceptable error range. Also, no filtration problems were accounted in acid leaching experiments due to formation of silica gel.

The undissolved residue, or secondary leach residue, of the optimum acid leaching experiment was analyzed for its zinc, lead, iron and cadmium contents, which were found to be 4.10 %, 19.17 %, 5.52 % and 85 ppm, respectively. Cadmium present in the blended leach residues was recovered at 84.3 % efficiency under the optimized acid leaching conditions. The results of hot sulphuric acid leaching experiments were consistent in general with those of previous researchers' [25 – 27].

When the XRD patterns of blended primary leach residues and secondary leach residue obtained at the optimum leaching conditions were compared for their constituents keeping in mind the change in weight due to leaching, it can be concluded that most of the zinc sulphate and some of the zinc ferrite as well as calcium sulphate were taken into the leach liquor during acid leaching as seen in Figures 4.6 and 4.7. In parallel to the decrease in residue weight, there was an increase in the amount of lead sulphate since it was insoluble in acidic media.

In other words, if initial and final residue weights were to be kept constant throughout the procedure, it could easily be seen that most of the initially present zinc sulphate and ferrite would vanish whereas the amount, therefore intensities, of insolubles like lead sulphate would increase because of the dissolved phases.

In the blended leach residues, $2ZnO.SiO_2$ was present in minor amount as stated before although it was not clearly detected in this study due to severe overlapping of the peaks of dominant phases like $PbSO_4$. Such a presence might have prevented the complete recovery of zinc.

Actually, it should be considered that the presence of acid insoluble zinc compounds not only zinc silicate but also complex zinc oxides reported by some researchers and interlocked or entrapped zinc ferrite within lead sulphate or other insoluble phases, might have limited the zinc recoveries at about 75 %. For this reason, experiments with much finer particle sized feed were performed.

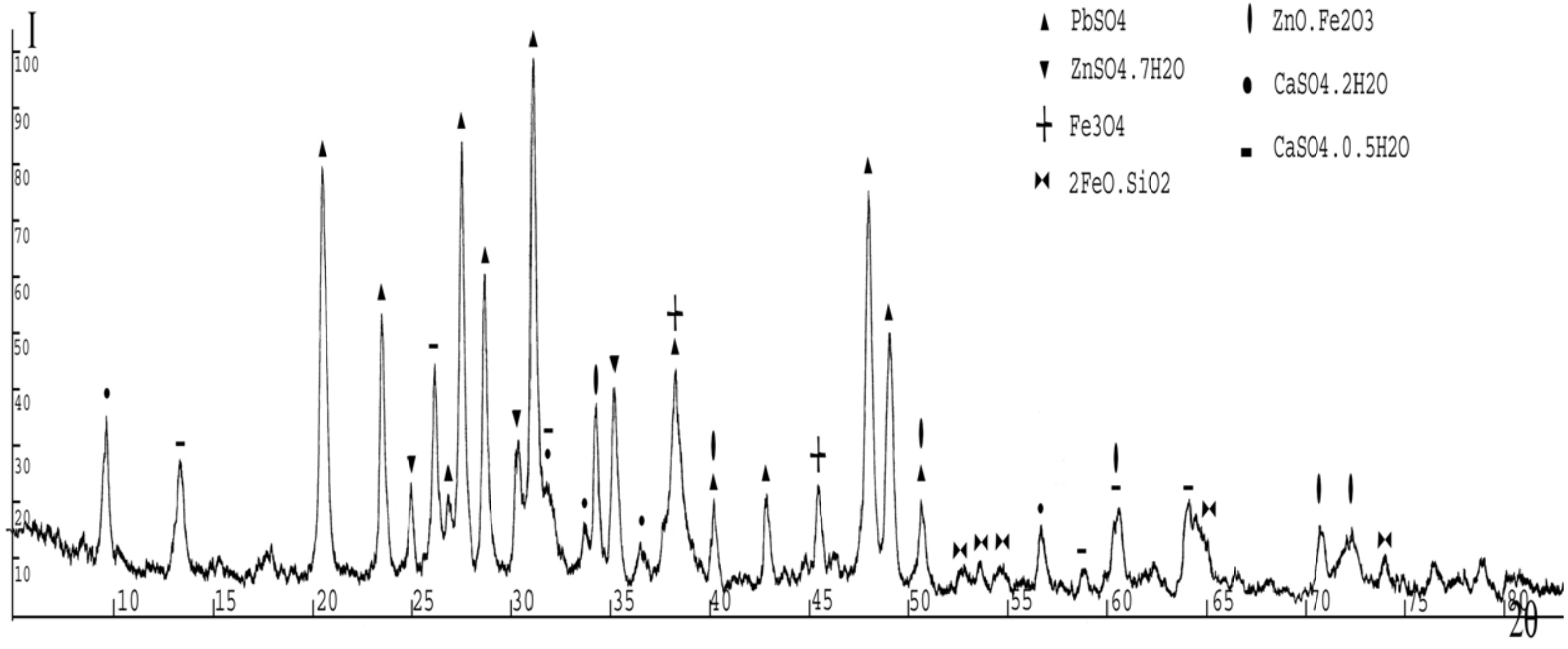


Figure 4.6 – XRD Pattern of Blended Leach Residue

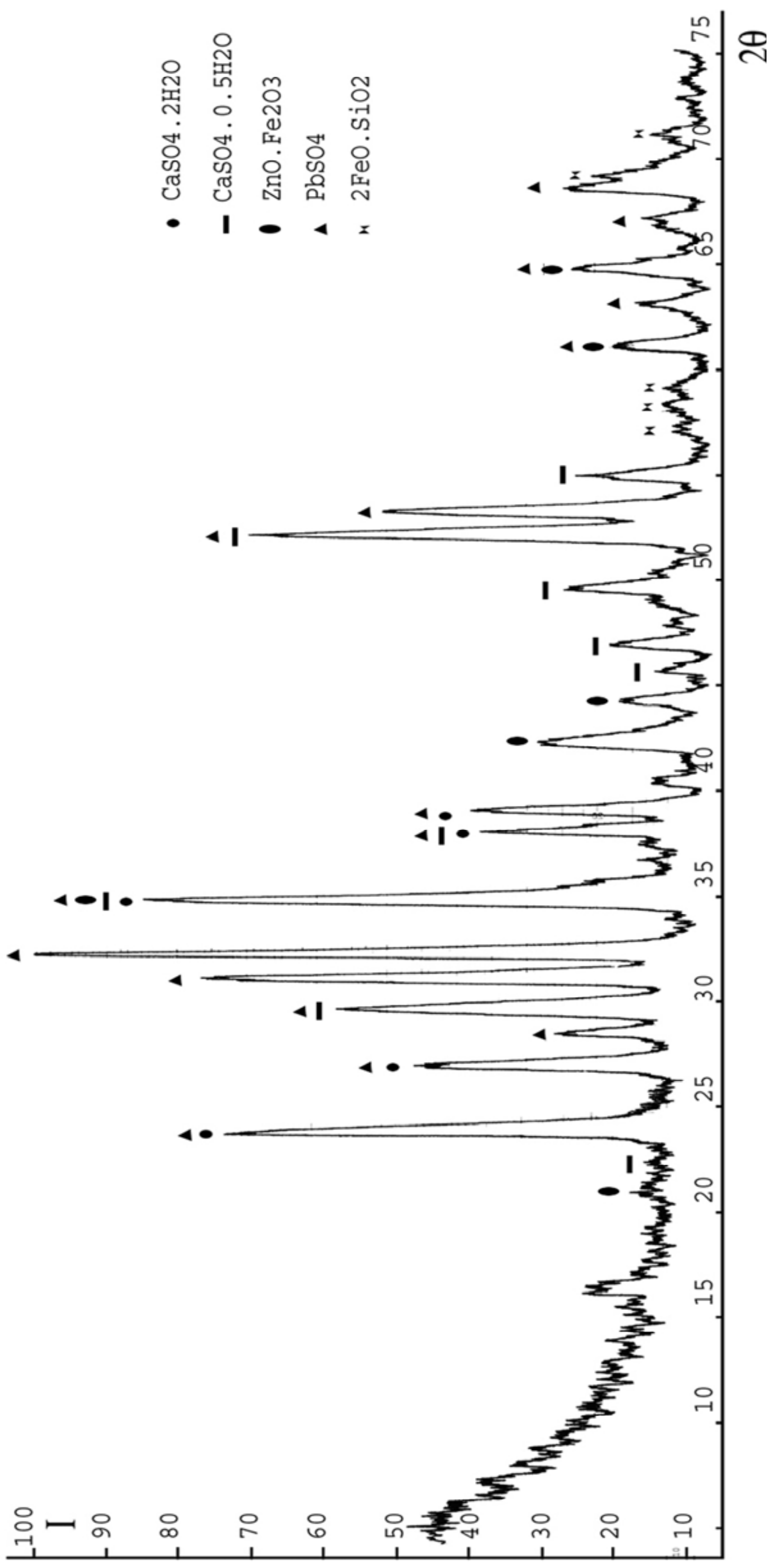


Figure 4.7 – XRD Pattern of Secondary Leach Residue of Acid Leaching

The pulverized original blended feed was further milled to a size of 89.5 % - 75 microns as previously done in water leaching tests. Unfortunately, only a 0.63 % increase in zinc recovery was obtained with a substantial increase in iron dissolution to 43.39 %. As a result, it was concluded that the energy consuming grinding operations would not be suitable for increasing the zinc recovery since there would be a further need for purification and investment in communition.

At the end, it can be said that the optimized conditions were applicable to the Çinkur plant where zinc content of residues could be converted to electrolytic zinc by installation of an additional hot acid leaching and iron precipitation unit. From the results, it should be noted that the amount of lead in the secondary leach residue was not suitable for sending to the already available lead smelter at Çinkur as concentrate. Thus, the secondary leach residue needed further treatment for lead recovery or to increase of its lead concentration to about 40% in order to be used as a feed to the short rotary kiln furnace available at Çinkur.

## 4.3. Brine Leaching Studies

By the hot acid leaching experiments mentioned above, it was shown that sufficiently high zinc as well as cadmium recoveries and some iron dissolution would be obtained as long as the optimum conditions were maintained. On the contrary, lead concentration of the secondary leach residue was not practically raised to an economically acceptable extent that were also mentioned as 40 % for the already installed Çinkur lead plant; consequently, this study was further expanded to recover or to convert the lead content of newly formed secondary waste into recoverable form.

Among the previous studies NaCl, $Na_2S$, $Na_2CO_3$ or NaOH treatments were mentioned and claimed to be promising for different residues [32, 36, 39, 40, 42]. From this information, as well as for its availability as the solvent medium to a very large extent and due to its relatively low price when other media were taken into account, in this study NaCl was chosen for lead recovery.

### 4.3.1. Effect of NaCl Concentration on Lead Recoveries

Previously, it was stated that most of the leaching procedures are time, temperature and concentration dependent. By considering this information, similar to acid treatment, the first experiments were done in order to determine the suitable NaCl concentration for brine leaching.

In all of the NaCl leaching experiments, as the raw material, the secondary leach residue stock was used. It was obtained by leaching of initial residue that was blended at 1/9 ratio of Iranian and Turkish leach residues at the optimum conditions of hot acid leaching. The pregnant acid leach liquor was then separated and the secondary leach residue was dried at 95°C after washing. At the end of drying, the secondary leach residue was ground to break up the agglomerates of which 88 % were less than 75 microns.

In determination of the suitable NaCl concentration, all the experiments were done at the predefined conditions of 30°C of leaching temperature, 15 minutes of reaction time and 250 g/l of pulp density. The results obtained are summarized in Table 4.6 and Figure 4.8.

Table 4.6 – Change of Recovery of Lead with NaCl Concentration in Brine Leaching

| **Experiment Code** | **NaCl Concentration (g/l)** | **Lead Recovery (%)** |
|---|---|---|
| BL 1 | 0 | 0.00 |
| BL 2 | 50 | 5.11 |
| BL 3 | 100 | 5.79 |
| BL 4 | 150 | 6.40 |
| BL 5 | 200 | 8.38 |
| BL 6 | 250 | 10.23 |
| BL 7 | 300 | 26.53 |
| Reaction Time = 15 minutes, Temperature = 30 °C, Pulp Density = 250 g/l | | |

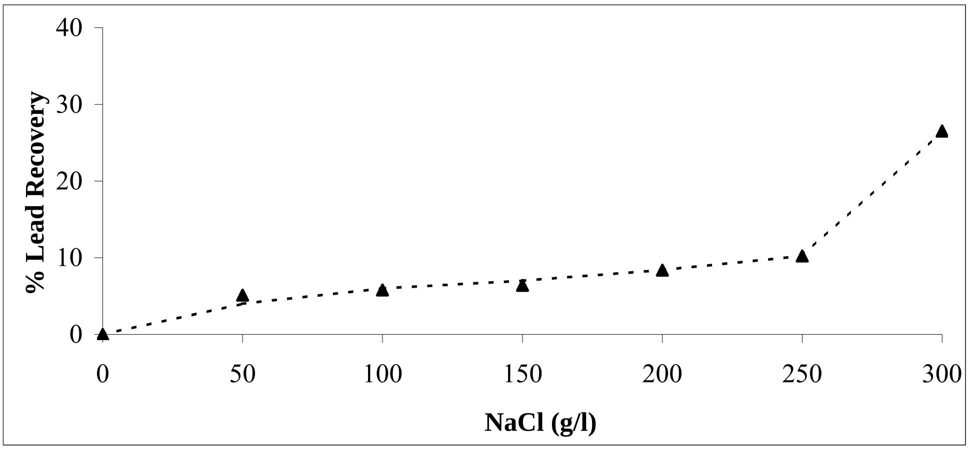


Figure 4.8 – Recovery of Lead vs. NaCl Concentration in Brine Leaching

Interpretation of data revealed that the lead recoveries did not go beyond 26.53 % by varying the NaCl concentration in a very wide range. More interestingly, there existed a sharp increase in lead recovery at 300 g/l NaCl concentration; however, it was thought that such an increasing trend would not continue at much higher concentrations as the NaCl solubility limit in water at 30°C is 335 g/l.

In the presence of high chloride concentrations, lead chloride subsequently converted to $PbCl_3^-$ and $PbCl_4^{2-}$ complexes having slightly higher solubilities [46]. Stoichiometric calculations, from the reactions corresponding solubility products of the above-mentioned complex lead ions (22 – 25), shown that lead in SLR completely dissolved and exhibited an extra dissolution at around 10 % as expected. That was the reason for higher lead extractions observed [50, 51] at high NaCl concentrations.

$$Pb^{2+} + Cl^- \rightarrow PbCl^+ \qquad K_{PbCl^+} = 10^{1.8} \qquad (22)$$

$$PbCl^+ + Cl^- \rightarrow PbCl_2 \qquad K_{PbCl_2} = 10^{0.18} \qquad (23)$$

$$PbCl_2 + Cl^- \rightarrow PbCl_3^- \qquad K_{PbCl_3^-} = 10^{-0.1} \qquad (24)$$

$$PbCl_3^- + Cl^- \rightarrow PbCl_4^- \qquad K_{PbCl_4^-} = 10^{-0.3} \qquad (25)$$

Just after defining the optimum conditions for NaCl concentration, effect of leaching temperature on the lead recoveries were investigated in 20 - 50°C range.

However, increasing temperature at 250 g/l pulp densities and 300 g/l NaCl concentrations did not give acceptable lead recoveries even though lead sulphate solubility increases with increasing temperature. This behavior can be explained by the presence of excess $PbSO_4$ or high pulp density in the leaching process. Since the leach liquor reaches its lead solubility limit, further dissolution of lead sulphate in limited amount of solvent was seemed to be unattainable.

### 4.3.2. Effect of Pulp Density on Lead Recoveries

The results of previous experiments showed the ineffectiveness of varying NaCl concentration. In fact, these findings were meaningful and in parallel with previous studies [29,44]. Nonetheless, most of the previous researchers had suggested the use of very low pulp densities or solid/liquid ratios such as 20 – 40 g/l. For this reason, as a part of sodium chloride leaching, the effect of pulp density on lead recovery was investigated.

In these experiments, the temperature and NaCl concentration were chosen as 20°C, 300 g/l, respectively so that the lead recovery values would be the highest for a leaching duration of 15 minutes. The results of these tests given in Table 4.7 and Figure 4.9 demonstrated that at very low pulp densities, the lead recoveries could reach acceptable levels around 82 %.

On the other hand, with increasing pulp density, the lead recoveries dropped sharply to below 30 %. This decrease in lead recovery with increasing pulp density was due to the limited solubility of $PbCl_2$ in the pregnant leach solution.

Table 4.7 – Change of Recovery of Lead with Pulp Density in Brine Leaching

| Experiment Code | Pulp Density (g/l) | Lead Recovery (%) |
|---|---|---|
| BL 11 | 20 | 81.98 |
| BL 12 | 30 | 73.71 |
| BL 7 | 250 | 27.42 |
| NaCl Concentration = 300 g/l. Reaction Time = 15 minutes, Temperature = 20 °C | | |

Although such reasonably high lead recoveries were obtainable by brine leaching at low pulp densities, the hydrometallurgical production of base metals is mostly economical at pulp densities in a range of 200 g/l to 300 g/l. The final residue that was obtained under the optimum conditions of brine leaching, i.e. at 20°C, 300 g/l NaCl, 15 minutes, 20 g/l pulp density with a final solution pH of 7.4 was analyzed for lead, zinc and iron contents and 7.87 % Pb, 6.86 % Zn, 8.79 % Fe were determined, respectively.

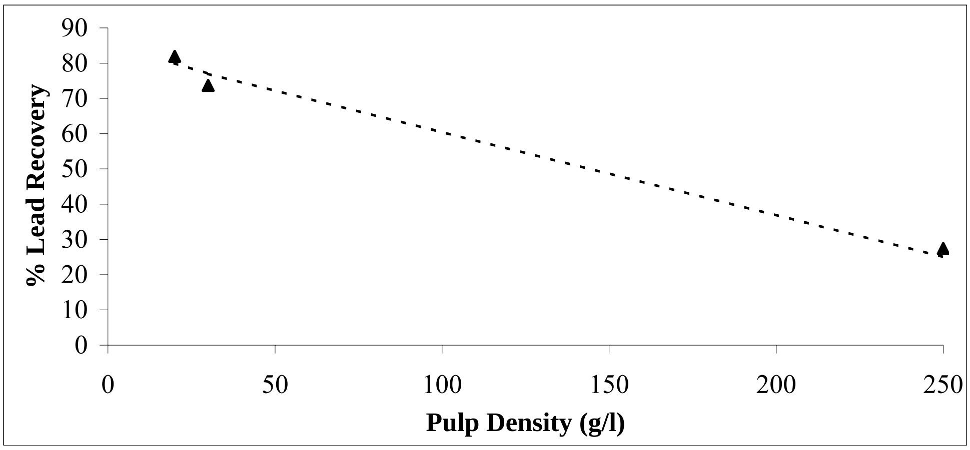


Figure 4.9 – Recovery of Lead vs Pulp Density in Brine Leaching

The XRD pattern of the final residue can be seen in Figure 4.10. As seen from the figure, the characteristic peaks of lead sulphate had disappeared from the XRD pattern, as a result of brine leaching. Some of the zinc ferrite and magnetite, which could not be leached either by acid or by salt, still showed up in the XRD pattern.

Since, the lead recovery values were very low in the first attempts for practical applications; further tests were done by changing the reaction time and particle size as the other parameters. In these sets of tests, reaction times of 5, 10, 15 and 30 minutes and particle size of 92.5 % below 75 microns at low pulp densities were investigated. From the results of these trials, it was seen that the lead recoveries did not change noticeably with increasing retention time or decreasing particle size. The highest recovery value was still not found satisfactory for further treatment by $Na_2S$ to convert $PbCl_2$ to PbS.

Thus, it could be concluded from the given results that NaCl treatment yielded a sufficiently high lead recovery value of about 82 %, reached at 20°C, 20 g/l pulp density and 300 g/l NaCl concentration in 15 minutes.

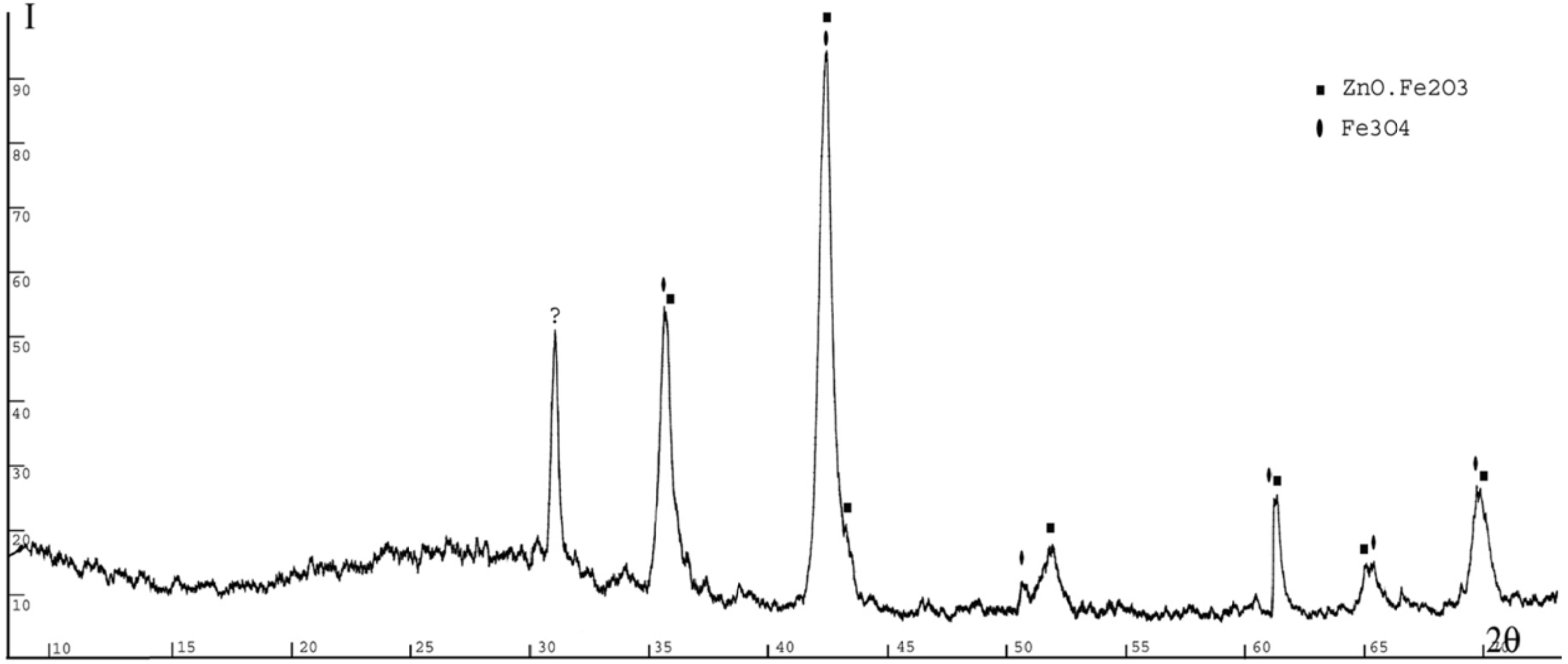


Figure 4.10 – XRD Pattern of Final Leach Residue

The results obtained may be considered unsatisfactory for industrial scale production, as it would consume vast amount of water and require large numbers of leaching tanks with low plant production capacity. However, in fact, sodium chloride leaching is the initial step of lead production from leach residues; the complete treatment requires the use of sodium sulfide in the following step as given below for the conversion of $PbCl_2$ to PbS, which could be shipped to lead smelters:

$$PbSO_4 + 2NaCl \rightarrow PbCl_2 + Na_2SO_4 \quad (17)$$

$$PbCl_2 + Na_2S \rightarrow PbS + 2NaCl \quad (18)$$

As can be expected, thus, the use of $Na_2S$ could increase the total treatment expenses though some of the NaCl would be recycled in continuous processes with the production of $Na_2SO_4$ as by-product.

Finally, while considering the overall applicability of the process, it should be stated that sodium chloride leaching might be a proper solution for lead recovery from the secondary leach residue if it is economical feasible. In the feasibility study, the evaluation must assume that NaCl recycling and $Na_2SO_4$ production as by-product would be achieved in up most efficiency to decrease extraction expenses that stem from the consumption of reagents and low productivity.

# CHAPTER 5

# CONCLUSIONS and RECOMMENDATIONS

Primary aim of this study was to recover the zinc and lead metallic values of the Çinkur leach residues. It was attempted to recover the mentioned metals as much as possible by hydrometallurgical processing routes, namely water, sulphuric acid and brine leaching methods. After the completion of physical, chemical and mineralogical characterizations of the residues, the leaching conditions were investigated thoroughly to obtain the highest metal recoveries. Because of the difference in origins, amounts and processing conditions, the physical, chemical and mineralogical properties of the Turkish and Iranian leach residues were different; hence, their responses to applied processes differed. To minimize behavioral differences and to obtain a homogeneous feed for consistent treatment, the leach residues were blended in 1/9 ratio according to their estimated amounts in Çinkur stockyard, i.e.,1 unit of Iranian and 9 units of Turkish leach residue. The blended leach residues contained 12.59 % Zn, 15.21 % Pb, 6.45 % Fe and 0.054 % Cd. Wet screen analysis of the same sample indicated that it was 63 % less than 75 microns.

Presence of water soluble phases like zinc and cadmium sulphates in the blended leach residue samples led to considerable discrepancies in determination of specific gravities.

From XRD and SEM results, it was seen that residues were composed of $PbSO_4$, $CaSO_4.2H_2O$, $CaSO_4.0.5H_2O$, $ZnO.Fe_2O_3$, $ZnSO_4.7H_2O$, $Fe_3O_4$ and $2FeO.SiO_2$. However, due to overlapping of the peaks of major phases on those of minor phases, whose existence was highly probable according to SEM results; kept some unidentified.

In water leaching experiments, it was proven once more that most of the zinc was present in the form of insoluble zinc ferrite in the blended leach residues. The highest achievable zinc recovery value by water leaching was found to be 10.26 % at 2 hours leaching duration, 95°C leaching temperature and 250 g/l pulp density with a final pH value of 5.9.

Hence, it can be suggested that if an additional fully-equipped water leaching unit were to be installed at an existing production line in the zinc plant, the production efficiencies would be increased by approximately 10 % by recovering zinc from the stock piled leach residues; in fact, by this unit when fresh residues are treated much higher recoveries can be expected.

Since water leaching did not give adequate zinc recoveries, sulphuric acid leaching was tried. First of all, sulphuric acid concentration was selected in such a range that the acidity of spent electrolyte would be suitable for leaching. Furthermore, the leaching duration and temperature directly affected the leaching of zinc, iron and cadmium from the blended leach residues so they had to be chosen accordingly while considering the purification expenses created by the dissolution of iron.

When the optimum hot acid leaching conditions determined as 150 g/l initial sulphuric acid concentration, 2 h reaction time, 95°C leaching temperature, 250 g/l pulp density with a final pH of 4.2 were maintained, it was found that the recoveries up to 74.87 % Zn, 39.59 % Fe and 84.3 % Cd could be obtainable while producing a secondary leach residue with the composition of 4.10 % Zn, 19.17 % Pb, 5.52 % Fe and 85 ppm Cd.

It can be stated that the optimized conditions seemed applicable and the zinc content of residues could be converted to electrolytic zinc by installation of a supplementary hot acid leaching and iron purification units, if current units would not be sufficient. The amount of zinc ferrite in the secondary leach residue could be lowered if the process was to be applied in continuous industrial operations where the probability of precipitation or re-formation of complex zinc compounds would be minimized.

The amount of lead in secondary leach residue of hot acid leaching was about 19 %, which was not suitable for shipping to lead smelters as concentrate, thus the secondary leach residue ought to be treated for lead recovery or concentration.

Once brine leaching conditions were optimized as 20°C, 300 g/l NaCl, 15 minutes and 20 g/l pulp density, the lead recoveries could reach acceptable limits around 82 %.

Under these conditions, the final residue contained 7.87 % Pb, 6.86 % Zn, 8.79 % Fe. Especially, with increasing pulp density the lead recoveries decreased to very low figures due to limited solubility of lead chloride.

Finer particle sizes and prolonged reaction times did not resulted in a considerable increase in lead recoveries. Moreover, higher NaCl concentrations were limited by the solubility of the reagent in water. Therefore, in brine leaching lead recoveries up to 82 % could be attained in laboratory scale. But, in industrial scale, due to consumption of vast amount of water, use of high numbers of leaching tanks and expensive reagents, the brine leaching procedure needed an economical evaluation for lead recovery.

At the end of this research, following suggestions can be made for future studies:

- After treating the blended leach residues with dilute hot sulphuric acid to leach out the acid soluble zinc and cadmium contents, the secondary leach residue can be treated directly with sodium sulphide solution to convert lead sulphate to lead sulphide.
- Various pyrometallurgical methods of metal extraction based on fuming of metal values should be tested on Çinkur leach residues. Especially, the application of Sirosmelt or Ausmelt technologies on the blended leach

residues should be given a priority. Alternatively, the use of plasma furnaces should also be kept in mind.

- In brine leaching, the effect of addition of HCl to the leaching media needs to be investigated. Especially, the effect of this addition on silver recovery from the blended leach residues should be studied.
- Leaching of blended leach residues using ammoniacal solutions such as ammonium sulphate, ammonium acetate, ammonium chloride and ammonium carbonate should be considered.
- Other leaching reagents like NaOH, $Na_2CO_3$ in order to obtain lead carbonate or lead hydroxide should be tested. Fusion or roasting with caustic soda followed with leaching need to be investigated.
- Precipitation and recovery of lead from lead chloride solution by $Na_2S$ or $Na_2CO_3$ to obtain PbS or $PbCO_3$ should be researched.
- Some of the processes developed for spent lead acid battery recycling can be applied to the leach residues in order to recover lead. Among the processes, PLINT Process is the first to be tested. By this hot brine leaching process, it may be possible to leach the lead present in the blended leach residues as $Na_2PbCl_4$ and to precipitate it as lead carbonate.

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