

68467

**GERMANIUM EXTRACTION  
FROM COPPER CAKE**

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



**BY**

**MEHMET KUL**

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE**

**DEGREE OF MASTER OF SCIENCE**


**IN**

**THE DEPARTMENT OF METALLURGICAL AND MATERIALS**

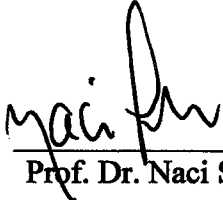
**ENGINEERING**

**SEPTEMBER 1997**


Approval of the Graduate School of Natural and Applied Science

  
Prof. Dr. Tayfur Öztürk  
Director

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



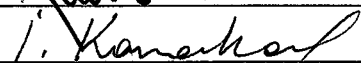

  
Prof. Dr. Naci Sevinç  
Head of Department

We certify that we have read this thesis and 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  
Prof. Dr. Gülhan Özbayoğlu  
Prof. Dr. Naci Sevinç  
Prof. Dr. İshak Karakaya  
Prof. Dr. Yavuz A. Topkaya

## **ABSTRACT**

### **GERMANIUM EXTRACTION FROM COPPER CAKE**

Kul, Mehmet

M.S., Department of Metallurgical and Materials Engineering

Supervisor: Prof. Dr. Yavuz A. Topkaya

September 1997, 89 pages

The main purpose of this thesis was to characterize and to extract germanium from the copper cake of Çinkur Zinc Plant. The physical, chemical and mineralogical characterization of the ground copper cake sample obtained from Çinkur showed that it was 84% below 100 Tyler mesh containing 700 ppm germanium. The copper cake also contained 15.33% Cu, 15.63% Zn, 1.66% Cd, 1.33% Ni, 0.64% Co, 0.35% Fe, 2.62% Pb, 12.6% As, 0.18% Sb and 3.42% SiO<sub>2</sub>. The mineralogical analysis indicated the complex nature of the copper cake which was mainly composed of metallic and oxidized phases containing copper, arsenic, zinc, cadmium, etc.

The sulphuric acid leaching experiments were performed under the laboratory conditions. The optimum extraction of germanium was obtained at a temperature range 60 to 85°C for a leaching duration of half an hour with sulphuric acid concentration of 150 gpl and using a solid/liquid ratio 1/4. Under these conditions, the recovery of germanium was 78% while the other metals were leached almost completely.

The precipitation of germanium was done from a stock pregnant leach solution containing 169 ppm Ge, 29.3 gpl Cu, 24.0 gpl Zn, 7ppm Pb, 867 ppm Ni, 491 ppm Co, 4.6 gpl Cd, 4.2 gpl Fe and 3.5 gpl As. As the precipitating agent for germanium tannin was used. With the increasing amount of solid tannin addition, there was an increase in the amount of germanium precipitated which reached a maximum value of 94 % for a mass of tannin that was 35 times the mass of germanium in the pregnant leach solution. One hour was found to be sufficient as the precipitation duration. The amount of germanium precipitated increased with increasing stirring speed up to 820 rpm from that speed onwards the increase in germanium precipitation was limited. The initial pH of the pregnant leach solution was also found to be important. Beyond a certain pH, precipitation of a solid phase high in arsenic was observed which was accompanied with a loss in germanium. The addition of tannin in the form of its solution instead of solid form was effective in the precipitation of germanium but the precipitate formed was more difficult to filter. The stagewise addition of tannin was also better than single step addition since the tannin consumption could be decreased in this manner.

Finally, it was decided that the best way to recover all the valuable metals present in the copper cake was to apply sulphuric acid leaching and then to precipitate from pregnant leach solution; the germanium with tannin in the first stage, copper with zinc powder or steel scrap in the second stage and consequently the zinc in solution could be precipitated as a hydroxide or recovered by electrowinning in the third stage.

Keywords: Copper cake, Germanium, Tannin, Sulfuric Acid Leaching, Precipitation.

## ÖZ

### BAKIR KEKİNDEN GERMANİYUM ÜRETİMİ

Kul, Mehmet

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü

Tez Yöneticisi: Prof. Dr. Yavuz A. Topkaya

Eylül 1997, 89 sayfa

Bu tezin ana amacı, Çinkur Çinko Fabrikasında ortaya çıkan bakır kekini karakterize etmek ve bu kekten germaniyum üretmektir. Çinkur'dan % 84'ü 100 meşin altında olmak üzere öğütülmüş olarak elde edilen bakır kekinin fiziksel, kimyasal ve mineralojik analizleri bakır kekinin 700 ppm germaniyum içerdiğini göstermiştir. Ayrıca bakır kekinde 15.33% Cu, 15.63% Zn, 1.66% Cd, 1.33% Ni, 0.64% Co, 0.35% Fe, 2.62% Pb, 12.6% As, 0.18% Sb ve 3.42% SiO<sub>2</sub> bulunmaktadır. Kompleks yapılı bakır kekinin mineralojik analizine göre bakır keki ağırlıklı olarak bakır, arsenik, çinko, kadmiyum, vb. metalleri içeren metalik ve oksit fazlarından oluşmaktadır.

Sülfürik asit liç deneyleri laboratuvar şartları altında yapılmıştır. Optimum germaniyum ekstraksiyonu 60 ile 85°C sıcaklıkları arasında yarım saat liç süresi ile 150 g/l sülfürik asit konsantrasyonu ve 1/4 katı/sıvı oranı kullanılarak elde edilmiştir. Bu şartlar altında germaniyum liç verimi % 78 iken diğer metallerin hemen hemen hepsi çözeltiye geçmiştir.

Germanyumun çöktürülmesi deneyleri 169 mg/l Ge, 29.3 g/l Cu, 24.0 g/l Zn, 7 mg/l Pb, 867 mg/l Ni, 491 mg/l Co, 4.6 g/l Cd, 4.2 g/l Fe ve 3.5 g/l As içeren stok liç çözeltisi ile yapılmıştır. Germanyumu çöktürme maddesi olarak tanin kullanılmıştır. Çözeltiye eklenen katı tanin miktarındaki artış ile çökelen germanyum miktarında artış gözlenmiştir ve bu artış liç çözeltisindeki germanyum miktarınının 35 katı tanin eklendiğinde maksimum değer olan %94'e ulaşmıştır. Çöktürme süresi olarak bir saatin yeterli olduğu bulunmuştur. Karıştırma hızındaki 820 devir/dakika'ya kadarlık artış ile çökelen germanyum miktarı artmıştır; fakat bunun üzerinde çökelen germanyum miktarındaki artış çok az olmuştur. Liç çözeltisinin ilk pH değerinin de önemli olduğu bulunmuştur. Belli bir pH değerinin üzerinde, yüksek miktarda arsenik içeren bir katı fazın çökeleği gözlenmiştir, bu çökelek germanyum kaybına sebep olmaktadır. Çözeltiye katı tanin yerine tanin çözeltisinin eklenmesi germanyum çöktürmesinde daha etkili olmuştur fakat; süzülmesi çok zor bir çökelek oluşmuştur. Taninin kademeli olarak eklenmesi tek aşamada tanin eklemekten daha iyidir çünkü, tanin tüketimi bu metod ile azaltılabilmektedir.

Sonuç olarak, bakır kekinde bulunan değerli metallerin kazanılması için en iyi yol önce bakır kekinin sülfürik asit ile liçi, daha sonra liç çözeltisinden metallerin çöktürülmesidir; ilk aşamada germanyum tanin ile, ikinci aşamada bakır çinko tozu veya hurda çelik ile çöktürülebilir, üçüncü aşamada ise çözeltideki çinko hidroksit olarak çöktürülebilir veya elektrokazanma yöntemi ile elde edilebilir.

Anahtar kelimeler: Bakır keki, Germanyum, Tanin, Sülfürik Asid, Liç, Çöktürme.

## **ACKNOWLEDGEMENTS**

The author wishes to express his sincere gratitude to Prof. Dr. Yavuz A. Topkaya for his valuable help in the preparation of this thesis.

Thanks are also due to Dr. Ahmet Çağatay for mineralogical analysis, Mrs.Serpil Şahin and Mrs. Selma Tan for chemical analyses, Mr. Cengiz Tan for SEM analysis of the copper cake and Dr. İbrahim Çam for XRD analyses of the copper cake. Special thanks are also due to Çinkur A. Ş. for providing the copper cake used in the experiments.

The author also wishes to acknowledge the help provided, in various aspects, by the staff of Mechanical Engineering Department of the Middle East Technical University, especially to Dr. A. Zafer Şenalp and Dr. Mehmet Çelik and to all of the colleagues and friends working in the Metallurgical and Materials Engineering and in the other departments.

## TABLE OF CONTENTS

	Page
ABSTRACT.....	iii
ÖZ.....	v
ACKNOWLEDGEMENTS.....	vii
TABLE OF CONTENTS.....	viii
LIST OF FIGURES .....	xi
LIST OF TABLES .....	xiv
CHAPTER	
1. INTRODUCTION.....	1
2. LITERATURE SURVEY.....	7
2.1. Extraction of Germanium.....	7
2.1.1. Mineral Processing Applications.....	10
2.1.2. Examples from Production Techniques.....	10
2.1.2.1.Recovery of Germanium from British Coals.....	13
2.1.2.2. Hydrometallurgical Techniques.....	13
2.1.2.3. Industrial Applications.....	14
2.1.3. Extraction of Germanium from Leach Solutions .....	30
2.1.3.1. Precipitation of Germanium from Leach Solution.....	33
2.1.3.2. Solvent Extraction of Germanium.....	35
2.1.3.3. Ion Flotation.....	36



2.2. Refining of Germanium.....	38
<b>3. EXPERIMENTAL SET-UP, PROCEDURE AND THE SAMPLE</b>	
CHARACTERIZATION.....	40
3.1. Experimental Set-up and the Procedure for the Leaching Experiments.....	40
3.2. Experimental Set-up and the Procedure for Tannin Precipitation	
Experiments....	42
3.3. Characterization of Copper Cake of Çinkur.....	44
3.3.1. Physical Characterization.....	44
3.3.2. Chemical Characterization.....	45
3.3.3. Mineralogical Characterization.....	45
3.4. Description of the Germanium Source of Çinkur Plant.....	57
<b>4. RESULTS AND DISCUSSIONS.....</b>	<b>59</b>
4.1. Leaching Experiments.....	59
4.1.1. Effect of Duration of Leaching on the Leach Recoveries of	
Metal Values.....	61
4.1.2. Effect of Acid Concentration on the Leach Recoveries of	
Metal Values.....	63
4.1.3. Effect of Temperature on the Leach Recoveries of Metal Values.....	65
4.1.4. Effect of Solid-Liquid Ratio on the Leach Recoveries of	
Metal Values.....	65
4.1.5. Effect of Chemical Oxidant and Air on the Leach Recoveries of	
Metal Values.....	68
4.1.6. Preliminary Studies in order to Overcome Leach Solution	
Filtration Problems.....	68

<b>4.2. Tannin Precipitation Experiments.....</b>	<b>70</b>
<b>4.2.1. Effect of the Amount of Solid Tannin Addition on the         Germanium Recovery.....</b>	<b>72</b>
<b>4.2.2. Effect of Tannin Precipitation Duration on the Germanium Recovery. .</b>	<b>73</b>
<b>4.2.3. Effect of Stirring Speed on the Precipitation of Germanium by Tannin.</b>	<b>74</b>
<b>4.2.4. Effect of pH Values of Solution on the Precipitation of         Germanium by Tannin.....</b>	<b>76</b>
<b>4.2.5. Effect of the Amount of Tannin Solution Addition on the         Precipitation of Germanium.....</b>	<b>77</b>
<b>4.2.6. Stepwise Solid Tannin Precipitation of Germanium.....</b>	<b>79</b>
<b>4.2.7. Effect of Air Blowing into Solution on the Germanium         Precipitation by Tannin.....</b>	<b>80</b>
<b>4.2.8 Precipitation of Other Metals by Zinc Addition into         Pregnant Leach solution.....</b>	<b>81</b>
<b>5. CONCLUSIONS.....</b>	<b>83</b>
<b>REFERENCES.....</b>	<b>86</b>

## LIST OF FIGURES

<b>FIGURE</b>	<b>Page</b>
2.1. Diagram of the Technological Process for Producing Germanium at the Tsume Plant.....	16
2.2. Diagram of the Hydrometallurgical Processing of Germanium Concentrates at Olen.....	18
2.3. Diagram of the Pyrometallurgical Processing of Germanium Concentrates at Olen.....	20
2.4. Diagram of the Processing of Dusts Rich in Germanium at Kolwezi.....	25
2.5. Flowsheet of Pertusola Crotone Plant.....	28
2.6. Daily Material Flow at the Vermont Plant .....	31
2.7. Diagram of the Recovery of Germanium from Zinc concentrates at Eagle-Picher Plant.....	32
3.1. Set-up of Leaching Experiments.....	41
3.2. Set-up of Germanium Precipitation by Tannin Experiments.....	43
3.3. X-Ray Diffraction Pattern of Copper Cake .....	47
3.4. Optical Microscope Photograph of Copper Cake : Cuprite.....	48
3.5. Optical Microscope Photograph of Copper Cake : Zincite.....	49
3.6. Optical Microscope Photograph of Copper Cake : Pyrite and Wustite.....	50
3.7. Optical Microscope Photograph of Copper Cake : Wustite and Cuprite.....	51

3.8. SEM Photograph of Copper Cake .....	52
3.9. SEM Photograph of Copper Cake .....	53
3.10. SEM Photograph of Copper Cake .....	54
3.11. SEM Element Mapping of copper Cake.....	55
3.12. SEM Element Mapping of copper Cake.....	56
3.13. Production of Copper Cake in Çinkur .....	58
4.1. Effect of Duration of Leaching on the Leach Recovery of Germanium.....	62
4.2. Effect of Duration of Leaching on the Leach recoveries of Other Metal Values .....	62
4.3. Effect of Sulphuric Acid Concentration on the Leach Recoveries of Germanium.....	64
4.4 Effect of Sulphuric Acid Concentration on the Leach Recoveries of Other Metal Values .....	64
4.5. Effect of Temperature on the Leach Recovery of Germanium.....	66
4.6. Effect of Temperature on the Leach Recovery of Other Metal Values .....	66
4.7. Effect of Solid-Liquid Ratio on the Leach Recovery of Germanium .....	67
4.8. Effect of Solid-Liquid Ratio on the Leach Recovery of Other Metal Values.....	67
4.9.Effect of Amount of Solid Tannin Addition on the Percent Precipitation of Germanium .....	73
4.10. Effect of Stirring Duration on the Percent Precipitation of Germanium .....	74
4.11. Effect of Stirring Speed on the Percent Precipitation of Germanium.....	75
4.12. Effect of Pregnant Leach Solution pH on the Percent Precipitation of Germanium.....	77

<b>4.13. Effect of Amount of Liquid Tannin Addition on the Percent Precipitation of Germanium.....</b>	<b>78</b>
<b>4.14. Effect of Stagewise Addition of Solid Tannin on the Percent Cumulative Precipitation of Germanium.....</b>	<b>80</b>



## LIST OF TABLES

TABLE	Page
1.1. The Minerals of Germanium.....	5
1.2. Physical Constants of Germanium.....	6
2.1. Recovery of Germanium at the Tsumeb Plant.....	17
2.2. Distribution of Elements in the Processing of Germanium	
Concentrates .....	21
2.3. Data on the Sulfate Roasting of Dust at the Kolwezi Plant.....	26
2.4. Laboratory Ion Flotation Conditions and Results.....	37
3.1. Dry Screen Analysis of Copper Cake.....	44
3.2. Chemical Composition of Copper Cake.....	45
4.1. Conditions of Copper Cake Leaching Experiments.....	60
4.2. Results of Copper Cake Leaching Experiments.....	61
4.3. Results of Germanium Precipitation by Tannin.....	71
4.4. Effect of the Amount of Zinc Powder Addition on the Percent Precipitation...	81

## CHAPTER 1

### INTRODUCTION

The existence of germanium was first suspected by Newlands (1864) as the missing member of the triad silicon, germanium, tin. Mendeleev (1871) recognized it as a missing element in his periodic table and predicted its general chemical properties from its relationship to silicon and tin. It was first isolated as the sulphide  $GeS_2$  from the rare mineral,  $Ag_8S_3Ge_3S_7$  by Winkler (1887) and named it 'Germanium' (Latin: Germania = Germany) in honour of his native country [1].

Although it was discovered in 1887 it had no usage industrially until development of transistors made up of germanium. Therefore, germanium was used as a semiconductor in the past but nowadays, its largest consumption area is optical uses such as fiber optics, infrared optics, microscope objects, wide angle lenses, ultra-violet and laser systems. Germanium is supplied to manufacturers in four wholly different forms: As a fairly pure for polycrystalline, elemental material for infrared lenses and windows, as a semiconductor of ultra-high purity for electronic devices, as spectrally pure germanium tetrachloride liquid for optical fibers and as pure germanium dioxide for catalysts [2].

The main use for germanium in 1978 remained in the field of semiconductor electronics. Its earliest use in 1941 was as a solid-state diode

performing as a detector in radar systems. This device was adapted to radio circuits as a radio-frequency detector, and the germanium transistor was invented in 1947. This invention revolutionized the electronics industry and caused a sharp increase in the demand for germanium. The use of germanium in these conventional semiconductors roles reached a peak in the early 1960s with world consumption averaging over 100 t/yr. Except for a brief upsurge in this demand during 1969, there has been a general decline in this usage since the early 1960s. In recent years, there has been an increase in the consumption of germanium due to the developments in germanium usage in the fields of infrared and fiber optic systems.

The use of germanium as a semiconductor substrate deserves special mention. In this use, semiconductor properties are not employed. In this application, single-crystal wafers of germanium are used as substrates for the epitaxial deposition of gallium arsenide/gallium arsenide phosphide for use as light-emitting diodes.

These substrates take the place of more expensive gallium arsenide wafers. At least one large company has made LEDs (light-emitting diodes) this way since 1974 [3]. A further significance of this application is that many people are considering this technology in the field of photovoltaic solar energy conversion. Although the use of Ge as a substrate for GeAs solar cells might save considerable GaAs, a recent study confirms that the use of germanium for this application would require many times the world's present production rate [4]. However, there are large, untapped sources of germanium and it is not inconceivable that such demands could be met in time with sufficient incentive.



The fastest growing use of germanium is in the field of IR optics. In this application, its transparency to IR wavelengths longer than 2  $\mu\text{m}$  and its high refractive index are utilized rather than its electrical properties. Other properties of advantage in this use are low dispersion, easy machinability, reasonable strength, low price compared to other IR materials, good resistance to atmospheric oxidation, to moisture, and to chemical attack, and availability in large sizes. It has been estimated that the world demand for germanium for IR devices will increase to 55t/yr during the 1980s [5]. Principal applications in this field are military. IR systems with germanium usually operate in the 8-12  $\mu\text{m}$  range and usually contain several germanium lenses, a germanium window, and a colour-correcting lens made from a Ge-Sb-Se glass or a Ge-As-Se glass. Some of the viewers also utilize a germanium IR detector for the sensor. Nonmilitary IR applications include lenses for CO<sub>2</sub> lasers, and windows for intrusion alarms. Germanium is also used as a thin film coating for IR materials to decrease reflection losses and/or to provide heavy filtering action below 2  $\mu\text{m}$ . Another application of germanium is the use of specially prepared germanium single crystals as gamma-ray detectors. Both the lithium-drifted detectors and the purer, more expensive, intrinsic detectors (which do not have to be stored in liquid nitrogen) do an excellent job of spectral analysis of gamma radiation and are important analytical tools. A significant use for germanium dioxide is as a condensation catalyst in the production of polyester fibers in which GeO<sub>2</sub> takes the place of cheaper Sb<sub>2</sub>O<sub>3</sub> to give a non-yellowing white fiber.

Other uses include the use of magnesium germanate as a phosphor, the application of niobium germanide as a superconductor, the addition of lead germanate to barium titanate capacitors, the use of bismuth germanium oxide

electro-optic crystals in diagnostic medical examination, the use of Ge-Au alloy in dental fillings and precision castings, the experimental use of organogermanium compounds in medicines, and the addition of GeO to glass formulations, primarily to increase the refractive index of the glass. A special example of this application is a recent development that shows considerable promise. This is the use of GeO<sub>2</sub> in fiber optics. In this application GeCl<sub>4</sub> is converted to GeO<sub>2</sub> which is deposited, along with SiO<sub>2</sub>, and sometimes B<sub>2</sub>O<sub>3</sub> and or P<sub>2</sub>O<sub>5</sub>, on the inside of a pure quartz tube and subsequently collapsed to form a solid rod or preform. The preform is then drawn into fine fibers which can be used as optical waveguides, primarily in the 0.8-1.6 μm wavelength region. Such fibers are proving increasingly useful in telephone lines, computer cables, and data transmission lines. There is considerable optimism concerning this application, and requirements of several tons Ge/yr by the early 1980s are predicted [6].

The biggest producers of germanium in the World are Belgium, USA, Germany and Italy, and the total world production amounts to over 80 tons per year. The estimated consumption pattern was as follows: Fiber optics 35%, infrared systems 20%, gamma ray + X-ray + infrared detectors 10%, semiconductors (including transistors, diodes and rectifiers) 10%, and other applications (catalyst, phosphors, metallurgy and chemotherapy) 25% [7].

It has been estimated that a ton of the Earth's crust contains from 4 to 7 grams of germanium. The minerals of germanium are quite few in number, but none of these minerals is presently utilised for recovery of germanium, presumably because of the small quantities available. Recovery of germanium from copper, zinc and lead

ores is economically feasible only because the germanium is concentrated in by-products during the process of recovering the primary metals; without such initial concentration of the germanium, it would not be economically possible to separate and purify it [8].

The minerals of germanium are quite few in number and those with the highest germanium contents are listed in Table 1.1 and its physical properties are presented in Table 1.2 [9].

Table 1.1. The Minerals of Germanium

Name	Composition	Germanium Content(%)
Germanite	$7\text{CuS}\cdot\text{FeS}\cdot\text{GeS}_2$	8.7
Argyrodite	$4\text{Ag}_2\text{S}\cdot\text{GeS}_2$	7.0
Renierite	$(\text{Cu,Fe,Ge,As})_x\text{S}_y$	7.0

In this thesis the possibility of recovery of germanium and the other metal values (Cu, Zn, Cd, etc.) from Çinkur solution purification precipitates (copper cake) has been studied. The first step in the metals recovery experiments was the characterization and sulfuric acid leaching of copper cake samples. After obtaining the pregnant leach solution with the optimum leach recoveries, the solution was treated by tannin in order to recover germanium by precipitation. The optimum precipitation conditions with tannin were determined by this study. On the other hand, the metal values other than germanium could be precipitated by zinc dust or scrap iron while the remaining solution could be advanced to leaching unit or to the electrolysis unit.

Table 1.2. Physical Constants of Germanium.

Atomic Number: 32
Atomic Weight: 72.6
<u>Isotopes and Abundance,</u>
Mass No 70 : 20.4%
Mass No 72 : 27.4%
Mass No 73 : 7.8%
Mass No 74 : 36.6%
Mass No 76 : 7.8%
Color: Silvery
Crystal Structure: Octahedral
Index of Refraction: 4.068 - 4.143
Ductility: Frangible
Density(g/cc)at 25°C: 5.32
Melting Point: 936°C
Boiling Point: 2700°C (approx.)
Latent Heat of Fusion(cal/g): 111.5
Latent Heat of Vaporization (cal/g): 1200
Specific Heat at 25°C: 0.086(cal/g)
Electrochemical Equivalent Ge <sup>+4</sup> (mg/coulomb): 0.1881
Electrode Potential Ge <sup>+4</sup> (H <sub>2</sub> = 0.0 volts): -0.15 (Estimated)

## CHAPTER 2

### LITERATURE SURVEY

#### 2.1 Extraction of Germanium

None of the minerals mentioned in the introduction chapter is mined solely for its germanium content. All of the germanium recovered worldwide is a by-product of other metals, mostly zinc, copper, and lead. The enriched copper-lead concentrates from Tsumeb have been treated in a vertical retort from which germanium sulfide is sublimed and separated. The Cu-Zn ores of Katanga (Zaire) have been treated by roasting with  $H_2SO_4$ , followed by leaching and selective precipitation of the germanium with MgO [10]. From the ores of Tri-State District in the United States, zinc concentrates are roasted and then sintered for zinc recovery. The sinter fume is chemically leached, and the germanium is selectively precipitated from the leach solution and sent to the germanium refinery. Germanium is also recovered from the still residue in the distillation of zinc metal [11].

In electrolytic zinc plants which are becoming increasingly important for environmental reasons, the germanium is separated chemically during the purification of the electrolyte prior to electrolysis. Germanium is one of several impurities that have an adverse effect upon zinc electrolysis. If the germanium concentration is high enough in the separated solids, economic recovery is possible.

Another example of the manufacture of germanium is from the British coals. Upon cooling of the combustion gases, germanium is deposited as a dust in the flues. Then, this dust is smelted to form a regulus, which is followed by distillation of  $\text{GeCl}_4$  upon addition of  $\text{HCl}$  [12].

Regardless of the source of the germanium, all germanium concentrates are purified by similar techniques. The ease with which concentrated germanium oxides and germanites react with concentrated hydrochloric acid and the convenient boiling point of the resulting  $\text{GeCl}_4$  ( $83^\circ\text{C}$ ) make chlorination a standard refining step. Chlorine is usually added to the primary distillation or to the subsequent fractionation, or both, to suppress the volatility of arsenic [13]. Other purification steps are used to separate certain other objectionable impurities if present. The fractionation is usually done in glass or quartz since the subsequent use of the germanium in electronics requires that the purified  $\text{GeCl}_4$  contain no more than about one mg/kg (1 ppm) impurities.

The purified  $\text{GeCl}_4$  is hydrolyzed with deionized water to produce  $\text{GeO}_2$  which is removed by filtration and dried. The dried  $\text{GeO}_2$  is reduced with hydrogen at about  $760^\circ\text{C}$  to germanium metal powder which is subsequently melted and cast into so called first-reduction or as-reduced bars. These bars are then subjected to zone refining to produce intrinsic or electronic grade germanium metal. Zone refining is ideally suited for the refining of germanium, and indeed, the original development of this procedure was caused by the need for ultra pure germanium [26]. Zone refining results in polycrystalline germanium usually containing less than 100 ng total impurities per g of germanium and less than 0.5 ng ( 0.5 ppb ) of electrically active

impurities per g Ge. For extremely high purity applications, such as for uncompensated gamma-ray detector crystals, germanium has been refined to impurity concentrations of less than 0.0003 ng/g (0.0003 ppb). However, zone refining is not equally efficient in removing all impurities. Boron and silicon are not removed easily this way and must be removed from germanium before the zone-refining step.

For its use as a semiconductor, refined germanium is grown into single crystals from the melt. The electronic properties are controlled by the addition of selected impurities (dopants) to the melt before crystal growth begins. The grown crystal is sliced and fabricated into devices, and the Ge scrap generated is recycled through the refinery into intrinsic germanium.

For its use in IR optics, zone-refined germanium is recast or grown into forms suitable for lens and window manufacture. After the germanium is annealed, it is cut and ground into lens or window blanks which are then polished, coated, and assembled into an IR system.

Environmentally, the production of germanium is quite harmless. Among the products produced, the chemicals consumed, and the by-products made, only arsenic would be considered a normal problem. The bulk of arsenic is separated from the germanium at the smelter, and small amounts entering the germanium-refining plant are easily controlled. The acids, bases, and chlorine used in processing and in gas scrubbing can be neutralized and held in permanent containment ponds. No hazardous substances are known to be discharged into surface waters or municipal treatment facilities from germanium-refining plants [14].

### **2.1.1. Mineral Processing Applications**

Very few copper, lead and zinc ores have been reported to contain germanium minerals which were treated by flotation and further concentrated to a higher grade germanium concentrate. As an example, germanium being in the form of germanite and renierite in the polymetallic Cu-Zn-Pb sulfide ores was upgraded to 0.2 - 0.42 % Ge from 0.053 % Ge by a flotation operation in Tsumeb Plant [15]. Also, in the Kipushi deposit of the Republic of Zaire, germanium exists in the form of inclusions of the mineral renierite which has ferromagnetic properties. In this process, the magnetic properties of renierite was used to separate it from the main body of the copper-zinc sulfide ores. Another example could be the selective flotation of renierite and copper which are associated with each other in Katanga deposit of the Republic of Congo [16].

### **2.1.2. Examples from Production Techniques**

Commercial recovery of germanium has been chiefly from zinc and zinc-copper-lead ores, germanite and flue dusts from coals. Ores from the Tri-State district (Missouri, Oklahoma, and Kansas) are concentrated and roasted to a crude zinc oxide by conventional means. Roasted ores mixed with salt and coal are sintered at high temperature; germanium, cadmium, and some other impurities are vaporized; and the vapours are condensed and collected in an electrostatic precipitator. This by-product fume is chemically treated to obtain crude fractions of germanium, cadmium and other impurities [13].



The germanium concentrate is reacted with strong hydrochloric acid. The resultant germanium tetrachloride {b.p. 83°C (187°F)} is distilled off. The crude tetrachloride is given additional purification and finally distilled with chlorine (to hold back arsenic). The purified, redistilled tetrachloride is then hydrolyzed in water to form germanium oxide, which is reduced to powdered metal by heating to 650°C in an atmosphere of hydrogen. The powdered metal is melted at 1100°C in an inert atmosphere to form ingots [13].

Zinc ores from the Mississippi Valley are concentrated, and the concentrate roasted and sintered in much the same fashion as the Tri-State ores; a by-product fume contains the recoverable germanium. This fume is leached with sulfuric acid under conditions which dissolve the zinc and cadmium and leave the lead, germanium, and other impurities as a sludge. The sludge is reacted with hot, strong sulfuric acid, the germanium in this liquor is precipitated with hydrogen sulfide, and the sulfide precipitated is roasted. The roasted material is then reacted with concentrated hydrochloric acid, and the distillation and purification are performed as described in the previous paragraph [13].

At Balen, Belgium, lead and zinc ores are smelted in a complex circuit; germanium is concentrated in a crude zinc oxide. Leaching of this crude zinc oxide under appropriate conditions dissolves the germanium. The germanium is precipitated, and the resulting germanium concentrate reacted with hydrochloric acid and distilled from the solution as germanium tetrachloride. Further purification steps follow essentially the same procedure as described for zinc ores [13].

The presence of germanium in zinc solution for electrowinning of the zinc is highly detrimental. This is one of the reasons for the separation of germanium in the electrolytic zinc plants. Another method for the purification of the zinc solution yields a sludge which contains the germanium, copper and arsenic. This sludge is smelted with excess sulfur to form a melt or molten matte substantially without the formation of metal or speisse layer in the melt. The melt is maintained in a molten condition to volatilize the germanium values therefrom as a fume after which said values are recovered from the fume [17].

At Tsumeb, Namibia, germanium occurs as germanite and renierite intimately mixed with the copper-lead-zinc ore of this district. By selective flotation a germanium concentrate is made, and the material is shipped to Olen, Belgium. Here the concentrate is processed in a vertical retort furnace under reducing conditions to obtain a germanium sulfide fume which is condensed. The fume is given an oxidizing roast; a crude germanium dioxide is obtained for the purification stage[13].

Germanium, as renierite, is dispersed through some of the copper-zinc ores from Katanga, Belgium Congo. In the flotation process for the concentration of these ores, the germanium follows the copper. During the smelting of the copper, dusts and fumes which contain appreciable amounts of germanium are collected. These fume and dusts are baked with sulfuric acid, and the baked dust is leached with weak acid to obtain a germanium-bearing solution. After oxidation of the solution, germanium is precipitated with magnesia and copper hydrate to give a concentrate for further purification [13].

At Tsumeb, in one process the pulverized germanite ore is reacted with 50 percent sodium hydroxide solution, and the mixture is evaporated to dryness. The dry mass is leached with hot water and the leach solution is brought to pH 3 with sodium hydroxide (to precipitate the gallium), the precipitate is filtered off, and the germanium is precipitated (as dioxide) by neutralization with ammonia. The germanium dioxide is then filtered from the solution and dissolved in strong hydrochloric acid, and the resultant germanium tetrachloride is distilled and purified. Hydrolysis of the tetrachloride to germanium dioxide and subsequent reduction and melting follow the same steps as previously described [13].

#### **2.1.2.1. Recovery of Germanium from British Coals**

Large quantities of British coals were used to make coke for producer gas plants. In the combustion of producer gas, germanium is largely volatilized. Upon cooling of the combustion gases, much of the germanium and some other metallic constituents are deposited as a dust in the flues. This flue dust is smelted with soda ash, lime, copper oxide and coal dust to form a regulus and a slag. The regulus, which contains most of the germanium, is reacted with chlorine under a dilute solution of ferric chloride and the crude germanium tetrachloride is distilled off [18].

#### **2.1.2.2. Hydrometallurgical Techniques**

It is important to note that each raw material for germanium recovery has its own set of problems in extractive metallurgy. Knowing also that the recovery of germanium alone does not seem to be economical, especially from zinc processing

residues hydrometallurgy could be more promising to recover most of the valuable metals from these residues. Those said processes can be summarized as leaching the germanium containing raw materials with 1.  $H_2SO_4$  alone 2.  $H_2SO_4 + HCl$  3.  $HCl$  etc., to get the germanium and the other metals into the solution. Most of the time, acid leaching of cement residues from zinc processing plants is carried out by using  $H_2SO_4$ , a low pulp density, relatively high temperature and moderately long leach times in agitation leach tanks. Among a number of studies concerning the optimization of leaching process for germanium bearing solution purification precipitates, Wardell and Davidson [19] has made an extensive research on leaching behaviour of zinc processing residues that contain an average of 0.46% Ge. The results obtained suggested that the roasting procedure prior to leaching with  $H_2SO_4$ , and  $SO_2$  has altered the form of germanium and made it more amenable to leaching[19].

### **2.1.2.3. Industrial applications**

Modern industrial production of germanium is based primarily on the intermediate products and wastes of the processing of polymetallic and zinc sulfide ores and coal. Plants using germanium-containing raw materials recover germanium as a by-product. The scale of its production from polymetallic sulfide ores at separate plants is small and usually does not exceed 2 to 3 tons per year. The production of germanium is organized on a large scale at the Lubumbashi-Kolwezi Plants in the Congo Republic and Tsumeb (Namibia) which ship their germanium dioxide concentrates to Belgium (Olen) for processing. The capacity of the Belgium plant

amounts to over 30 tons of germanium per year [20]. In the USA, germanium is obtained as a by-product of the processing of zinc ores. [16]

The polymetallic sulfide ores processed by the Tsumeb concentrating plant contain 41 ore minerals [20]. In these ores, germanium is present in the form of two minerals, germanite and renierite, which differ in their flotation properties. The principal mineral is germanite, but it is intimately intergrown with minerals such as galena, tennantite, sphalerite and dolomite, [21] so that in order to sort out the germanium minerals, it is necessary to pulverize the ore down to 20  $\mu\text{m}$ . Renierite possesses magnetic properties, which are used to determine the quality of the germanium concentrate obtained. The movement of a magnet under glass causes a displacement of renierite, and the rate of this movement (under the microscope) indicates the extent of enrichment of the sample by germanium.

The plant adopted a process for separating the germanium concentrate from copper-lead-zinc concentrates (Figure 2.1). The copper-lead concentrate, from which zinc has been removed, is stirred for 10 minutes with a solution of starch and sulfur dioxide at  $\text{pH} = 5.2$  in a conditioning tank. The rougher flotation of germanium is then carried out, most of the metal being removed as a frothy product, from the first three chambers. The concentrate of the rougher flotation is treated with limestone for 10 minutes and recleaned in an open cycle at  $\text{pH} = 10.0-10.5$ . The rougher germanium concentrate is thus obtained. The tailings of rougher and recleaner flotation consist of the copper-lead concentrate. Table 2.1 shows the recovery indices of germanium [22]. The recovery of germanium in the concentrate amounts to over 28% for an enrichment by a factor greater than seven. The concentrate obtained in the

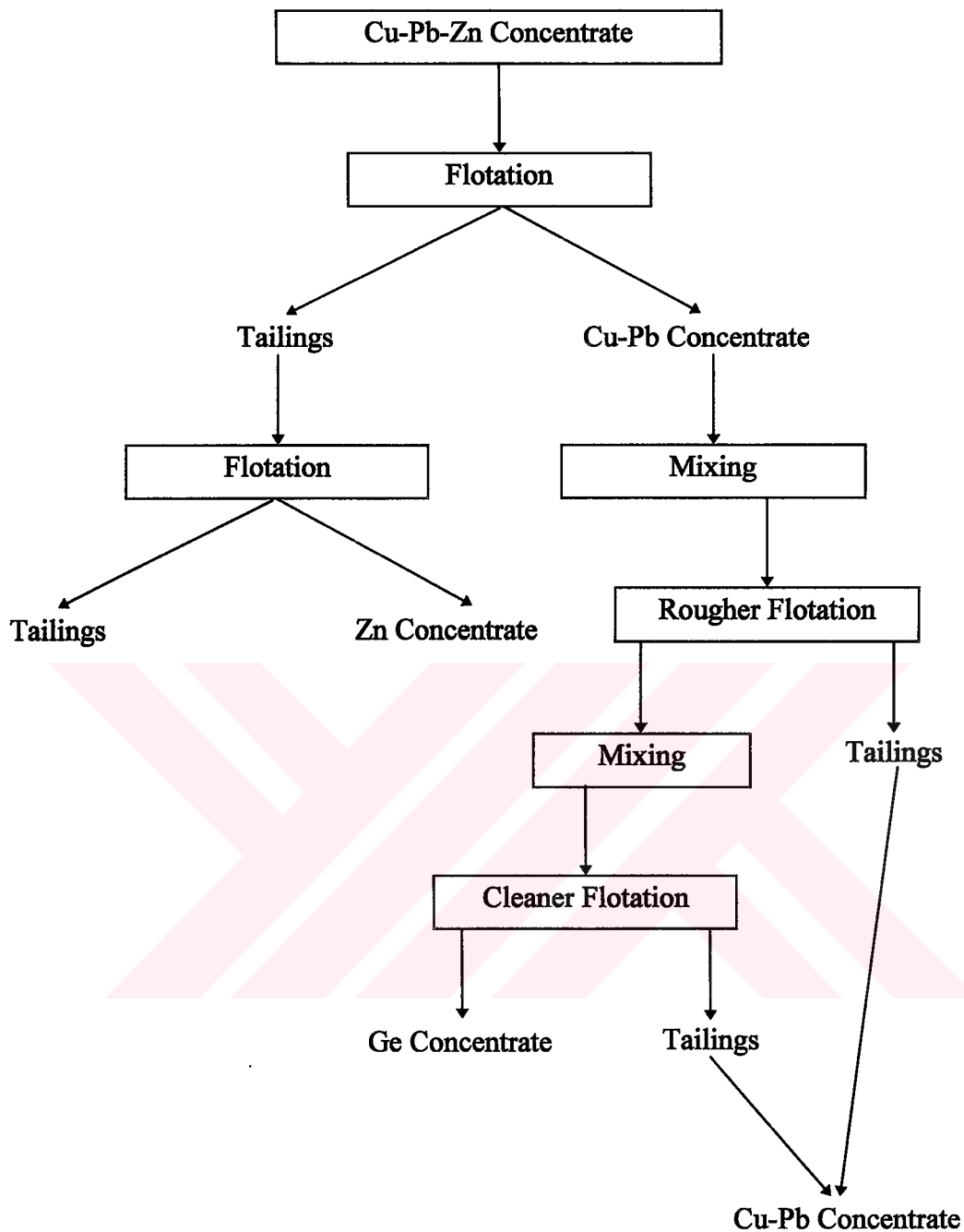


Figure 2.1. Diagram of the Technological Process for Producing Germanium at the Tsumeb Plant

plant, containing 0.20-0.45% germanium, is shipped for further treatment to the former radium plant at Olen, Belgium.

Table 2.1. Recovery of Germanium at the Tsumeb Plant.

Product	Yield, %	Content, %			Recovery, %		
		Cu	Pb	Ge	Cu	Pb	Ge
Initial Cu-Pb Concentrate	100	11.83	56.6	0.053	100	100	100
Germanium Concentrate	4	26.54	23.3	0.385	9.07	1.59	28.1
Cu-Pb Concentrate	96	10.72	57.94	0.039	90.93	98.41	71.9

During the first few years, the Tsumeb germanium concentrates were treated at Olen by the wet process (Figure 2.2). The oxidizing roasting of the concentrate was carried out in reverberatory furnaces. Subsequent leaching of the sinter caused up to 90% of the germanium to go into solution. The leaching was carried out in two stages.

The concentration of sulfuric acid in the solution after the second stage of leaching was 50 g/l, whereas after the first stage it was 5-10 g/l. The solution, containing 5.6g/l germanium, was evaporated until the concentration increased tenfold, and was cooled with vigorous stirring. Germanium tetrachloride was then distilled out of the thick slime obtained. The wet process was simple and was carried out with standard equipment. However, the production losses were high and the recovery was not sufficient.

In a number of American laboratories, studies were carried out for the purpose of developing a process that would be more suitable for the treatment of the germanium flotation concentrate [21]. Three processes were proposed and tested on a small scale. Two are based on the use of caustic soda for leaching germanium: One involves leaching in an autoclave; the third, preliminary pelletizing and sintering on a

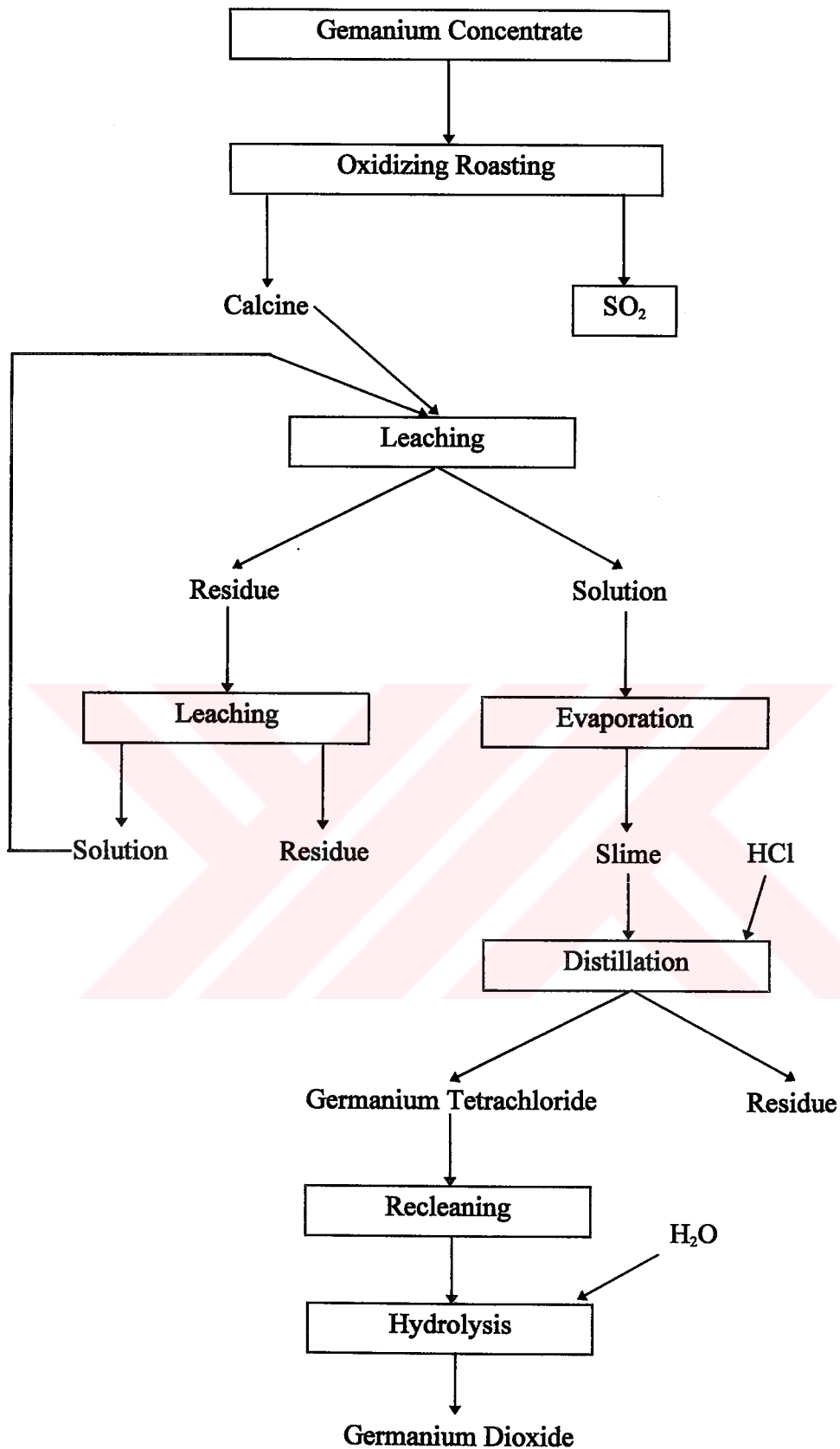


Figure 2.2. Diagram of the Hydrometallurgical Processing of Germanium Concentrates at Olen.



belt. The third process is based on the volatilization of the sulfides, followed by the extraction of germanium into the condensate and distillation of germanium tetrachloride.

The Belgian company which treats the germanium flotation concentrate also developed a new process using a vertical retort for volatilizing the sulfides (Figure 2.3). The temperature of the retort process is determined by the requirement of minimum losses in the sublimates.

In an atmosphere of carbon monoxide or flue gas at a temperature of about 900 °C, the volatilization of germanium sulfide reaches 90-93%, and that of lead sulfide 5-10%. After drying to a moisture content of 2%, the charge is briquetted. Prior to charging into the retort, 4% wood charcoal or 10% coke, relative to the weight of the concentrate, is added to the briquets. This increases the porosity of the charge and prevents its fusion.

The vertical retort furnace is an open-flame muffle furnace with a built-in retort made of carbon brick. The briquets are charged periodically from above by means of a charging mechanism and are lowered into the reaction zone. The gas obtained from wood charcoal (average composition: 28-30% CO, 1-2% H<sub>2</sub>, balance nitrogen) is passed through the retort from the top downward. The gases containing the volatilized sulfides are passed through a water-cooled condenser and cloth dust-collectors. The sulfide residue is discharged through a mobile feeder into a closed container. The average temperature of the reaction zone is 870-980 °C, and the gas temperature is 700°C. The sublimate collected from the condensers and dust

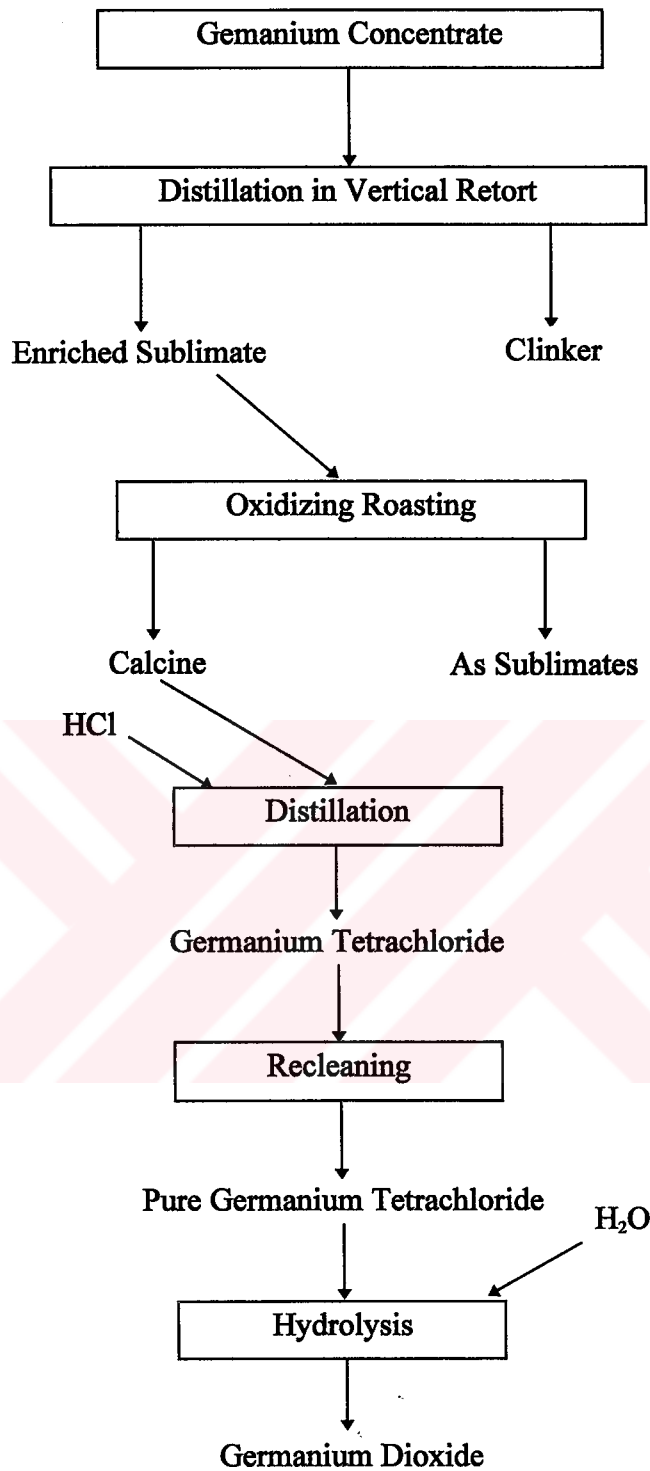


Figure 2.3. Diagram of the Pyrometallurgical Processing of Germanium Concentrates at Olen.

collectors is roasted in electric furnaces. The roasting is conducted at 550°C in order to oxidize as much of the sulfur as possible, and to drive off the arsenic as the trioxide. The oxide residue is treated, then germanium tetrachloride is distilled. The result of the treatment of germanium concentrates by volatilization of the sulfides are shown in Table 2.2. The total recovery of germanium by the plant using this process is 90%.

Table 2.2. Distribution of Elements in the Processing of Germanium Concentrates.

Product	Yield,%	Content %			Distribution %		
		Ge	As	Pb	Ge	As	Pb
Ge Flotation Concentrate	100	0.25	7.5	26	100	100	100
Sulfide Calcine	85	0.03	0.15	28.8	8.3	1.7	94.2
Oxide Residue	2.7	8.5	32.2	55.5	91.5	1.1	5.7
Arsenic Sublimate	9.7	0.01	75	0.15	0.2	97.2	0.1

Whatever the manner in which they were obtained, the germanium concentrates are subjected to distillation in which germanium is driven off as the tetrachloride. The distillation process is carried out with a 9 N hydrochloric acid solution in the presence of chlorine. The latter is necessary to oxidize the arsenic, and also antimony and bismuth. If the chlorination is carried out without free chlorine, arsenic trichloride (boiling point 130°C) is volatilized together with germanium tetrachloride (boiling point 83°C). The chlorination is conducted in an insulated vessel. The primary stills are glazed steel boilers of 200-liter capacity with steam jackets provided with stirrers and discharged through the bottom. The lids have holes for Pyrex distillation columns and inlets for chlorine and the acid. At the start of the operation, the material is charged into the still and mixed with concentrated

hydrochloric acid and various circulating solutions. Chlorine is introduced without being preheated until it saturates the solution, then germanium tetrachloride is distilled in a moderate stream of chlorine. The vapours condense in a Pyrex condenser cooled to  $-10\text{ }^{\circ}\text{C}$  by circulating brine. The condensed tetrachloride is collected in 75-liter Pyrex flasks provided with mechanical stirrers and is subjected to chemical purification. Each steel condenser-collecting vat-cleaning bottle train operates as an independent unit. In order to prevent the loss of tetrachloride, each vat containing  $\text{GeCl}_4$  is connected to a condenser in which the temperature is  $-10^{\circ}\text{C}$ . All the effluent gases are washed with sodium carbonate in a tower of 1.2 m in diameter and 6.5 m high. The spent solution is periodically recycled.

The chlorination compartment contains rubber lined settling tanks with a mechanical stirrer for the treatment of the various by-products. Germanium is recovered from the latter by neutralizing the hydrochloric acid solution with limestone.

Germanium tetrachloride is purified in a separate section of the plant where the oxide is produced, All of the equipment in this section is made of quartz or a special plastic. Following chemical purification, germanium tetrachloride is subjected to fractional distillation.

When germanium dioxide is precipitated by hydrolyzing the purified tetrachloride, the stirring, the rate of addition of the tetrachloride to doubly distilled water, and the temperature of the process are closely controlled. After filtration and washing, germanium dioxide is dried at  $200^{\circ}\text{C}$  in an electric furnace.

Of major importance in the production of semiconducting germanium is the maintenance of a high degree of purity in the course of the production process; this is accomplished by using special structural materials and by taking special precautions against external contaminants. All the working areas are provided with forced ventilation. An "absolute" filter of high efficiency for small sizes of the trapped particles is used to purify the air. Particularly high requirements are set for the purity of the air used to force the liquids into the bottles. The floors, walls and work clothes in the sections of germanium oxide production are covered with a special composition. The paint used for coating the metal parts of the equipment must not contain any inorganic dyes. The water is purified in ion-exchange columns filled respectively with activated carbon and cation- and anion-exchange resins. The specific resistance of the water thus obtained is  $5 \times 10^6$  ohm/cm. The preparation of germanium metal and its refining will be discussed below.

The copper-zinc sulfide ores of the Republic of the Congo are characterized by a high content of germanium. Rich copper ore (up to 20% Cu) and copper flotation concentrates are treated by the copper smelting plant in the town of Lubumbashi (near Elizabethville) [21]. In certain Katanga ores, germanium is found in the form of inclusions in the mineral renierite. In selective flotation, renierite is primarily associated with copper minerals. For this reason, following selective flotation, the bulk of the germanium present in the copper-zinc sulfide ores of the Republic of the Congo is subjected to smelting with copper concentrates.

The copper smelting plant at Lubumbashi has an annual capacity of 120000 tons of crude copper. The main technological process of the plant includes sintering,

semipyrritic smelting of the sinter in shaft furnaces, and purging of the matte in the converter. In shaft smelting, germanium distributes itself between the matte, the slag and the dust. The matte is fed into the converter, where part of the germanium escapes with the dust. The slags of shaft furnaces, containing zinc, cadmium and germanium, are stored.

The metallurgical dusts trapped by the cloth dust collectors consist of a complex raw material containing zinc, cadmium and arsenic. They are shipped for treatment to a zinc electrolysis plant located in the vicinity, in the town of Kolwezi.

The dust-processing plant in Kolwezi was put into operation in 1955; its planned capacity is 590 tons of dry dust per month. The annual output is 220 tons of dry concentrates containing 8-10% germanium or 25-31 tons of germanium dioxide. The average recovery of germanium from the processing of dusts is about 75%; the after-treatment recovery by sintering attains 92%, and leaching and precipitation produce over 80%. A flow diagram of the dust-processing plant is shown in Figure 2.4.

Prior to sulfate roasting, the dusts are mixed with sulfuric acid (60-100% of the weight of the dust) and water on a screw feeder. The mass has a moisture content of 25-30%. The sulfating is carried out in a rotary furnace 1 m in diameter and 22 m long for 4 hours at 450-500°C. The furnace has an acid-resistant lining. As a result of the sulfate roasting, most of the arsenic is driven off. Table 2.3 lists data on the loss of elements associated with sulfate roasting.

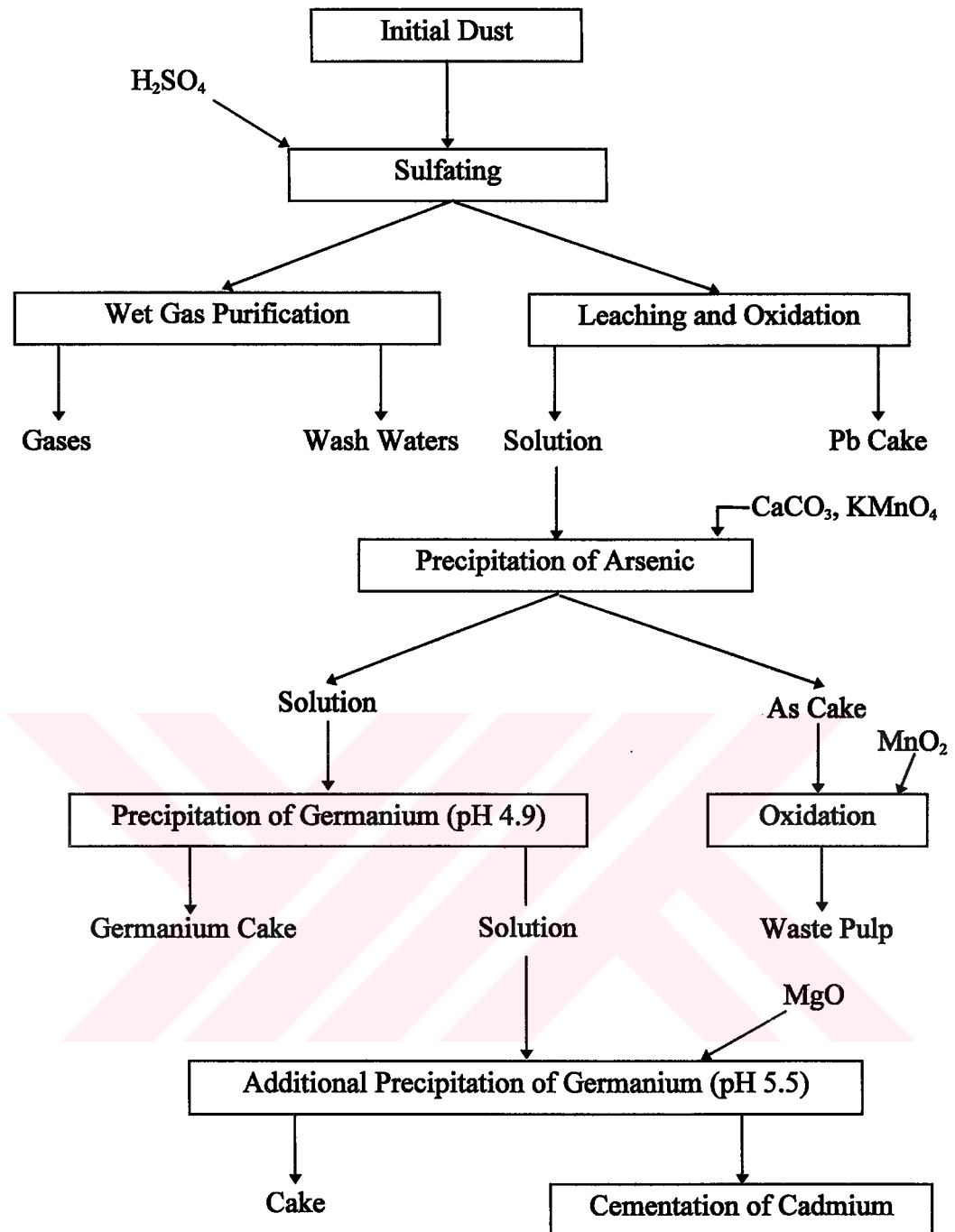


Figure 2.4. Diagram of the Processing of Dusts Rich in Germanium at Kolwezi

Before being discharged into the atmosphere, the gases leaving the furnace are washed in scrubbers. The cake is transferred into a hammer mill in order to pulverize the lumps formed.

Table 2.3. Data on the Sulfate Roasting of Dust at the Kolwezi Plant.

Element	Content in dust, %		Loss due to roasting, %
	Initial	Roasted	
Germanium	0.36	0.285	8
Zinc	28	22.5	6
Cadmium	3	2.64	5
Lead	25	20.3	3
Copper	1.5	1.2	0
Arsenic	7.3	0.7	88-90

The leaching is carried out in agitators (each having a 42-m<sup>3</sup> capacity) lined with lead for 1.5 hours. At the same time, 9-10 tons of the charge is introduced. Leaching involves the use of a sulfate solution consisting of a mixture of the spent electrolyte from the electrolysis of cadmium and of wash waters from the filtering operation at the last stages of the process. The final acidity of the solution is 10-15 g/l, and its composition at the end of leaching is ; 110-130 g/l Zn, 15-20 g/l Cd, 2.5-4 g/l As, 1.4-2 g/l Ge, 2-4 g/l Cu . The average recovery by leaching is 98-99 % Zn, 94-96 % Cd, 80-85 % As, 90-95 % Ge, 75-90 % Cu and 78-80 % Fe. After the pulp has settled, an oxidizing agent is added to the clarified solution. The pressed pulp is filtered on filter presses. The residue is lead cake (61.5% Pb, 1.28 %Zn, 0.5 % Cd, 0.83 % Cu, 0.39 % As, 0.05 % GeO<sub>2</sub>).

The oxidizing agent used is anodic slime from electrolysis, which contains a large amount of manganese oxide. In order to complete the oxidation, excess potassium permanganate is added. The oxidation operation lasts 1.5 hours at 45°C.



The oxidation operation is accompanied by a partial precipitation of arsenic in the form of arsenates of iron and other metals; the arsenic concentration drops to 1.5-2.0 g/l. At this stage of the process, the solution is adjusted to pH 2.3-2.4 by the addition of pulverized limestone. The pulp is filtered and washed on filter presses, then the solution is sent to the section where germanium is precipitated. The arsenic content of the solution is less than 0.4 g/l, that of iron 100 mg/l, and that of copper 3-5 g/l.

Germanium is precipitate in two stages, at first only a part of germanium is precipitated, in order to obtain a pure product. In the first precipitation of germanium, magnesium oxide is added until the pH is 4.9. The second stage of precipitation is carried out at a higher pH, and the precipitate is returned to the preceding stage. The cake obtained from the first stage of precipitation contains 8-10 % Ge, 15-20 % Zn, 1-1.5% Cd, 10-18 % Cu, 0.7-2.0 % As. This product is dried and shipped to the refining plant at Olen. The low grade germanium precipitate obtained from the second stage is concentrated and shipped without filtration to the cadmium cementation section of the zinc electrolysis plant. Its composition is; 110-120 g/l Zn, 12-18 g/l Cd, 1-3 mg/l As and 15-36 mg/l Ge [16].

One more example could be Pertusola Plant in Italy. This plant has originally been designed to treat zinc sulfide concentrates, with 0.013-0.014% Ge, in order to produce electrolytic zinc. The flowsheet of this plant is shown in Figure 2.5. In this process, the zinc sulfide concentrates are first converted to oxide by roasting and then they are leached to obtain an electrolyte with the required degree of purity. In order to

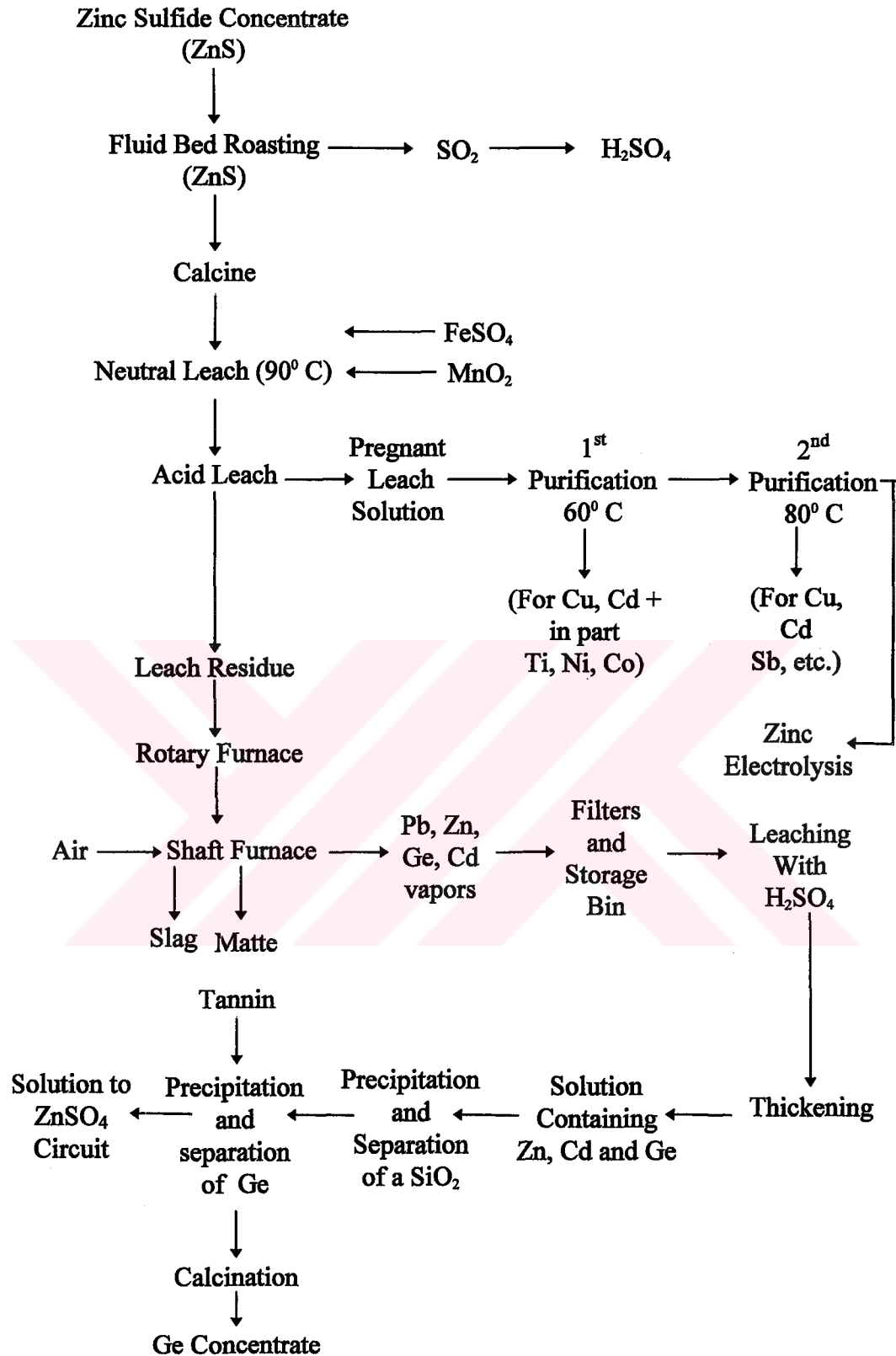


Figure 2.5. Flowsheet of Pertusola Crotone Plant.

purify the solution zinc dust is added and most of the detrimental impurities are precipitated. Later the leach residue is charged to a rotary furnace and then it is

smelted in a shaft furnace whereby obtaining the vapors of Pb, Zn, Cd, containing 0.08 - 0.15% Ge and a matte-slag system. Subsequently, the vapors are condensed and leached with sulfuric acid in order to get Zn and Ge into the solution. The insoluble part is  $\text{PbSO}_4$ . The precipitation of  $\text{SiO}_2$  from solution is followed by the precipitation of germanium by using tannin. Consequently, the solution contaminated with tannin is neutralized and advanced to the  $\text{ZnSO}_4$  circuit. The germanium tannin compound is washed, filtered, dehydrated and calcined in a furnace. As a result, a germanium dioxide concentrate containing about 30% Ge is obtained [23].

The zinc ores of the USA also serve as a source material for the industrial production of germanium. Given below is a description of the technological process used in the production of germanium at a zinc plant in Vermont, where from 4.5 to 7 kg of germanium dioxide is obtained daily. The main raw material used by this plant are zinc concentrates whose germanium content reaches to 400 g/t. The bulk of concentrates contains 40-100 g of germanium per ton. The average content may be assumed to be 100 g/t.

In the course of the oxidizing roasting and sintering of the concentrate, most of the cadmium, germanium and lead concentrate in the fumes and dust; these products are sent to the cadmium plant. Cadmium and zinc are leached out by weak acid solution.

Germanium is leached out of the lead cake with hot concentrated sulfuric acid, and is then precipitated as a sulfide cake. After oxidizing roasting, the cake is

washed away from the cadmium by acid, and germanium tetrachloride is distilled (Figure 2.6) [21].

Another plant where germanium is obtained from zinc concentrates, located in Henrietta (Oklahoma), belongs to the Eagle-Picher company. Here (Figure 2.7), the zinc concentrates are roasted in order to oxidize the sulfide. Coal and sodium chloride are then added to the calcine, and the sintering is carried out at a high temperature. Cadmium chloride and germanium chloride are vaporized; the sublimate is then subjected to further treatment [24].

### **2.1.3. Extraction of Germanium from Leach Solutions**

Essentially, all hydrometallurgical germanium recovery processes involve getting the germanium into the solution and the treatment of pregnant leach solution with various chemicals in order to extract the germanium values from the solution selectively. Thus, two important topics are discussed below, concerning the recovery of germanium from leach solution. The selection of the most suitable technique depends highly on the type of the solution, i.e., concentration of germanium in the solution and other constituents of the solution. Generally, the input to solvent extraction is a leach solution containing relatively high concentrations of germanium (i.e., 1 gpl Ge). But KELEX-100 was found promising even at relatively lower germanium concentrations (i.e., 0.2 - 0.3gpl). On the other hand, tannin precipitation would be employed to treat those solutions with much lower concentrations of germanium.

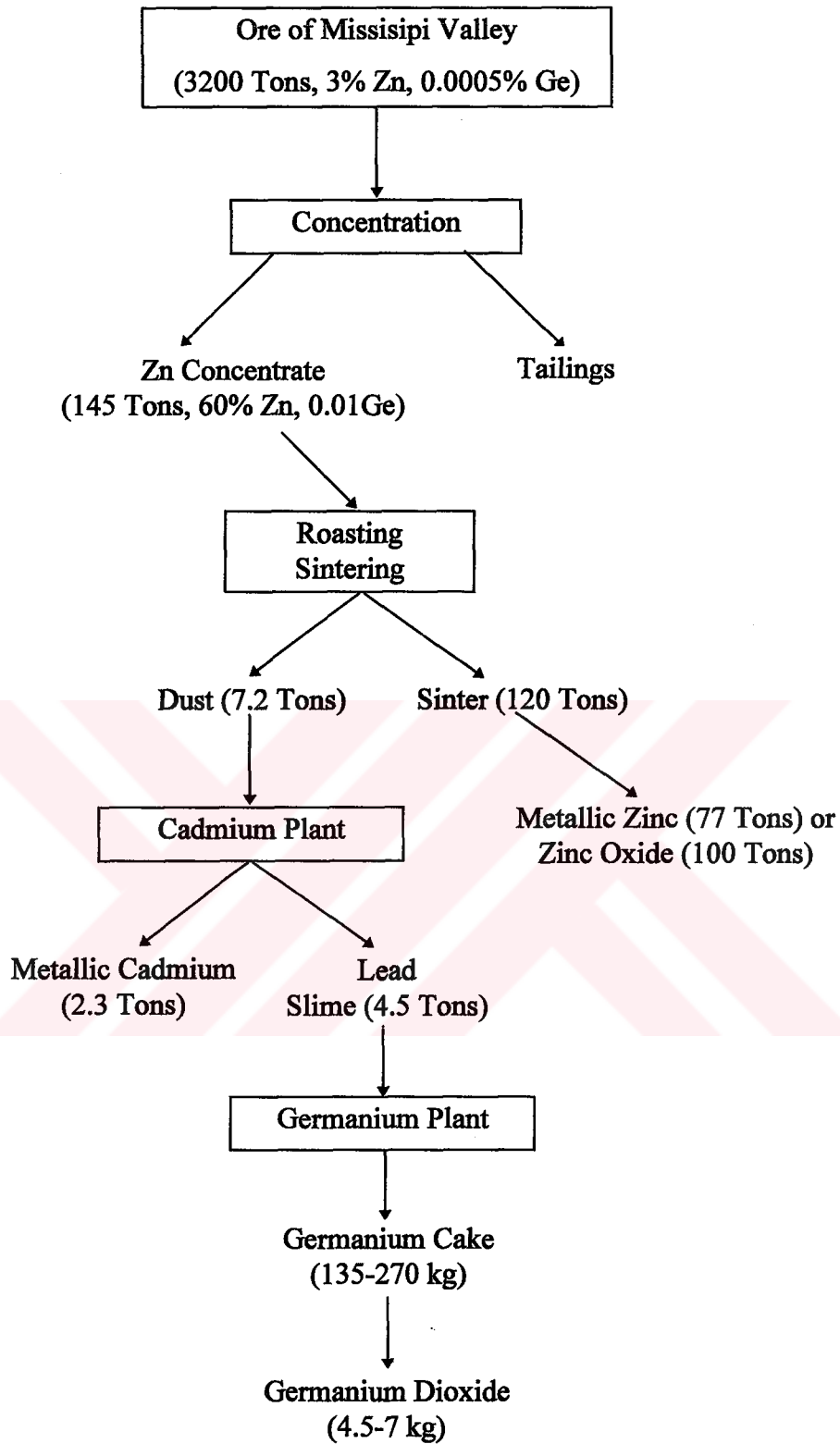


Figure 2.6. Daily Material Flow at the Vermont Plant

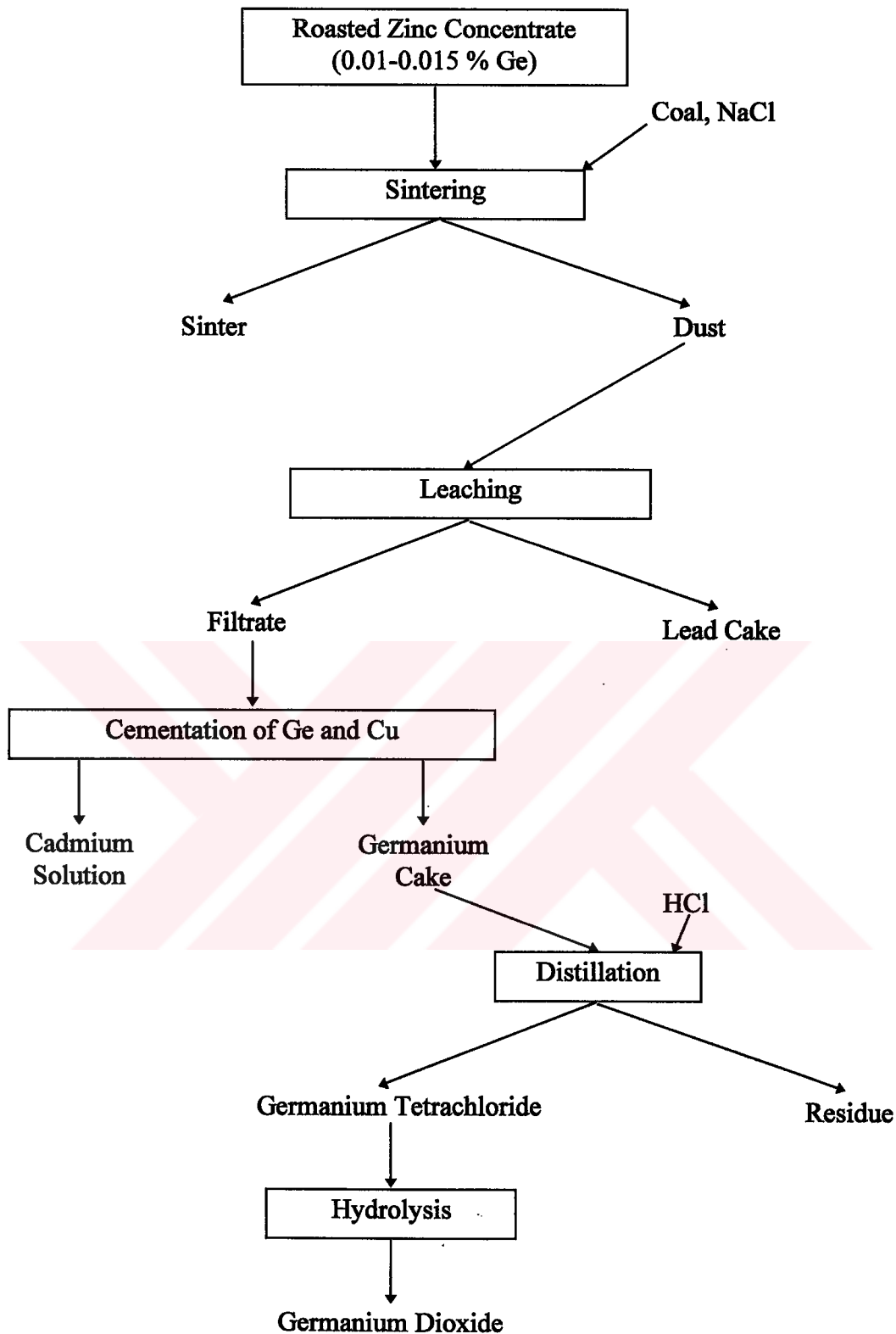
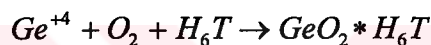


Figure 2.7. Diagram of the Recovery of Germanium from Zinc concentrates at Eagle-Picher Plant

### 2.1.3.1. Precipitation of Germanium from Leach Solution

Chemical precipitation methods are used to treat the leach solution containing relatively low concentrations of germanium, i.e., less than 1 gpl [25]. Those chemical substances making strong compounds with germanium, are added to the pregnant leach solution and germanium is precipitated in the form of insoluble complexes. Tannin ( $C_{76}H_{52}O_{46}$ ) is generally employed for leach solutions containing very low concentration of germanium while for higher concentrations  $H_2S$  and Zn are preferred. The pertinent reaction for tannin precipitation of germanium can be written as;



where T represents the Tannin ( $C_{76}H_{52}O_{46}$ ) with molecular weight of 1700 [26]. Since the atomic weight of germanium is 72.6, the stoichiometric tannin requirement is 23.4 times the mass of germanium present in solution.

Tannin precipitation process is widely employed in the industry but requires a solid tannin addition of 30 times the mass of germanium in solution. Moreover, the pH of the solution should be about 2. After the precipitation is complete, the germanium-tannin compound is filtered and collected. The efficiency of this process varies between 78-100% . On the other hand, upon addition of tannin, the solution becomes contaminated whereby creating problems in the following zinc electrolysis. In addition to tannin;  $H_2S$  and zinc, MgO and  $Ca(OH)_2$  can also be used in order to precipitate germanium from leach solutions [27].

Some examples from the industrial applications of chemical precipitation methods are as follows; at Kolwezi as explained in section 2.1.2, produces germanium precipitate in two stages, at first only a part of germanium is precipitated, in order to obtain a pure product. In the first precipitation of germanium, magnesium oxide is added until the pH is 4.9. The second stage of precipitation is carried out at a higher pH. The cake obtained from the first stage of precipitation contains 8-10 %Ge, 15-20 % Zn, 1-1.5% Cd, 10-18 % Cu, 0.7-2.0 % As. This product is dried and shipped to the refining plant at Olen.

The low grade germanium precipitate obtained from the second stage is concentrated and shipped without filtration to the cadmium cementation section of the zinc electrolysis plant. Its composition is ; 110-120 g/l Zn, 12-18 g/l Cd, 1-3 mg/l As and 15-36 mg/l Ge. Another example is the Katanga deposit of the Republic of Congo where MgO is used for precipitation of germanium from the leach solution [6]. The major user of tannin for the precipitation of germanium is the Pertusola-Crotone zinc plant in Italy, as it is explained in section 2.1.2 [23].

Another precipitation method of germanium with tannin is the stepwise addition of tannin, if the starting material is the residue from a zinc circuit neutral leach. The procedure of this method is the following :

1. Leach the solution purification precipitate or residue with hot  $H_2SO_4$  to solubilize the germanium, then adjust the pH to 1.0 with zinc fume and filter to remove the solids.



2. To the filtrate from Step 1, add tannin solution (100 grams/liter deionised water, then filter) in order to precipitate the germanium. This is done in three steps to conserve the amount of tannin required.

2A. For the first step, use a tannin to germanium mass ratio of 8/1 and filter.

2B. For the second step, use a tannin to germanium mass ratio of 12/1 and filter.

2C. For the third step, use a tannin to germanium mass ratio of 16/1 and filter.

3. Combine the three germanium-tannin precipitates on a filter and wash with methanol to improve purity.

4. Roast the germanium-tannin precipitates at less than 600°C to produce a GeO<sub>2</sub> concentrate.

After conversion to the oxide by roasting, a concentrate containing from 5-20% germanium, as germanium dioxide, is produced. This concentrate is the feed to the conversion reaction [28].

#### **2.1.3.2. Solvent Extraction of Germanium**

The electrolysis of zinc can be achieved with a good yield only when germanium has been completely eliminated from the electrolyte. This separation is therefore a preliminary operation to the recovery of zinc metal from solution. Moreover, the recovery of germanium from such solutions constitutes the main available source of this metal. Liquid-liquid extraction and resin separation methods appeared to be attractive and have been widely studied . Various solvents such as carbon tetrachloride, chloroform, tributylphosphate and extractants such as long

chain amines, alkylphosphoric acids, phosphinic acids, oxine, hydroxamic acids and alkylpyrocatechol as well as many resins, e.g. AN-31, EDE-10P, Dowex-1, Amberlite XE-243 and silica gel have been proposed. However, the low capacity of most resins and extractants, their prohibitive cost and the strict separation conditions have often limited their application. The  $\alpha$ -hydroxyoxime compounds, especially LIX 63 (later replaced by LIX 26), has been proposed and tested by Metallurgie Hoboken-Overpelt, Belgium. LIX 63 has further been used in a semi-industrial plant for a couple of years but at the moment Hoboken-Overpelt Plant is recovering germanium from leach solutions by an organic that has been developed after many years of research and its formula has not yet been disclosed [29]. Actually there are, at the moment, three important organic solvent extraction reagents in use either in pilot plant stage or in industrial application. They are KELEX 100 in France [13], H -106 developed in USA [30] and that unknown organic reagent developed in Belgium.

### **2.1.3.3. Ion Flotation**

Germanium recovery method from leach solutions explained so far, are accompanied by several disadvantages. These are consumption of costly reagents and energy, laborious and lengthy operations (as in settling, filtration and dewatering of slimes). Also the use of tannin for precipitation of germanium, contaminates the leach solution thereby creating problems in zinc electrolysis. Known characteristics of ion flotation are its effectiveness, simplicity, relative cheapness and fast treatment of large volumes containing low concentrations [28]. Although no commercial process based on ion flotation has been reported, the laboratory experiments of ion flotation was found promising under the conditions given in Table 2.4. The typical

initial concentration of germanium in the solution was  $10^{-4}$  M (or 0.0073 gpl) and pyrogallol was used as a ligand (flotation activator) while the surfactant was laurylamine at specified pH's of the solution. From these experiments [31], ion flotation of germanium was reported to be sensitive to the ionic strength of solution, studied by the addition of ammonium salts. The relation found regarding the recovery decrease was  $PO_4^{-3} > SO_4^{-2} > Cl^{-}$ . A pH correction and the use of surfactant, in excess, in this case was observed to improve flotation. Consequently, removals of over 90% were obtained at neutral pH conditions and stoichiometric addition of the flotation reagents.

Table 2.4. Laboratory Ion Flotation Conditions and Results

Test Volume		100 cm <sup>3</sup>
Ge initial		1*10 <sup>-4</sup> M
Pyrogallol/Ge		Three times
Dodecylamine/Ge		Twice
Reagents excess		10%
Ethanol		0.5%
pH		7
Stirring		No
Nitrogen flow rate		3.33 cm <sup>3</sup> /s
Pressure difference		26.6kN/m <sup>2</sup>
Retention time		300 s
Ge recovery		>90 %
Flotation rate		1 st order

## 2.2. Refining of Germanium

Whatever the manner in which they were obtained, all germanium concentrates are treated with similar techniques, i.e. they are subjected to distillation by which germanium is driven off as the tetrachloride. The distillation process is carried out with a 9N hydrochloric acid solution in the presence of chlorine. The latter is necessary to oxidize the arsenic, and also antimony and bismuth. If the chlorination is carried out without free chlorine, arsenic trichloride (b.p.130°C) is volatilized together with germanium (b.p.83°C) [9]. After distillation of  $\text{GeCl}_4$  is complete at the required purity, the hydrolysis of  $\text{GeCl}_4$  is performed in order to convert it into  $\text{GeO}_2$  precipitates in accord with reactions (1) and (2).



In considering the hydrolysis reactions, it is important to remember that hydrolysis ceases at an acidity of approximately 7.8M HCl. In 5.5M HCl, soluble germanium is present as germanic acid. In practice, a ratio of three grams of water per gram of germanium tetrachloride yields a germanium dioxide recovery of approximately 95% with the balance reporting as soluble germanic acid. By operating at 0°C and allowing a small amount of material to precipitate and act as nucleation centers, prior to reducing the bulk of the tetrachloride, both high yield and acceptable

bulk density can be achieved. Then the germanium dioxide is suction filtered and dried at 100°C. The final step is the calcination of dried GeO<sub>2</sub> at 300 - 400°C [32].

As the higher purity GeO<sub>2</sub> is obtained, it is transferred to reduction section where GeO<sub>2</sub> is reduced by H<sub>2</sub>. The pertinent reactions are as follows:



The first step involves reducing germanium dioxide to the monoxide compound while the second step reduces the monoxide to metal. The germanium recovery of this process is usually between 98 and 99%.

The final step in the production of intrinsic semiconductor grade germanium is premelting and zone refining [32].

## **CHAPTER 3**

### **EXPERIMENTAL SET-UP, PROCEDURE AND THE SAMPLE CHARACTERIZATION**

In this chapter, the experimental set-up used in the leaching and precipitation experiments as well as the experimental procedure followed are explained. The physical, chemical and mineralogical characterization of the copper cake used in the germanium recovery experiments are also described. Description of the germanium sources at Çinkur zinc plant are also given.

#### **3.1. Experimental Set-up and the Procedure for the Leaching Experiments**

In the leaching experiments a hot plate with contact thermometer and a magnetic stirrer was used. The leaching was done in 250 cc glass balloons using Teflon coated magnets. A condenser attached to the balloon prevented the vaporization losses and with the aid of the contact thermometer, the temperature of the system was controlled within  $\pm 2^{\circ}\text{C}$ . The leaching set-up used is shown schematically in Figure 3.1.

In order to recover germanium and the other valuable metals from the copper cake, a series of experiments were done by using the mentioned set-up. At the end of each leaching experiment, the insoluble leach residue was separated from the pregnant leach solution by passing it through a filter paper and the solids were

washed with distilled water in order to obtain the leach residues as free from the pregnant leach solution as possible.

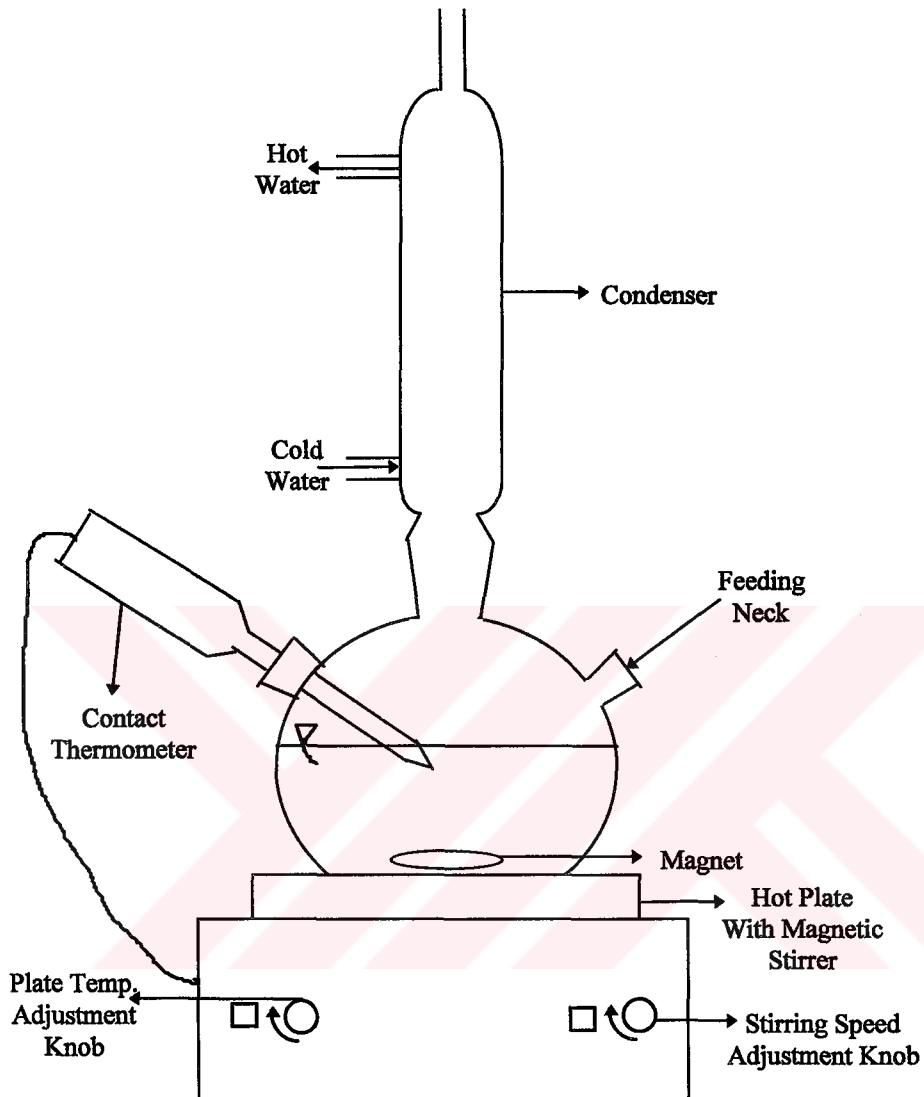


Figure 3.1. Set-up of Leaching Experiments

In the leaching tests the procedure followed was as follows: A measured amount of distilled water and calculated amount of pure Merck quality sulphuric acid were put into the glass balloon and heated to the desired temperature while magnetically stirring. Then, the weighted amount of copper cake was added to the

dilute sulphuric acid solution and the timing was initiated. The stirring speed which gave sufficient mixing was kept constant in all the experiments. At the end of leaching duration, solid-liquid separation by filtration followed as explained above. The washed leach residues obtained were dried, weighted and analyzed by Perkin Elmer Model 2380 AAS (Atomic Absorption Spectrophotometer) for germanium and the other valuable metals.

The leach recoveries were calculated using the analysis of the copper cake and the leach residue and their respective masses.

### **3.2 Experimental Set-up and the Procedure for Tannin Precipitation Experiments**

Experiments involving the precipitation of germanium by the addition of solid or liquid tannin were done by use of a 600 cc beaker, a mechanical stirrer with adjustable speed, a filter funnel, an air blowing pump and filter papers. The experimental set-up used in the precipitation experiments is shown in Figure 3.2.

On the other hand, the procedure followed in tannin precipitation was as follows: A measured amount of pregnant leach solution which was produced during the pilot plant leaching of copper cake at Çinkur was placed in the beaker. All of the precipitations were done at room temperature. Since the amount of germanium in the pregnant leach solution was known before hand, the calculated amount of solid tannin was added to the pregnant leach solution and mechanically mixed by a stirrer at a predetermined speed. The duration of precipitation was started from the moment



that the tannin was added to the solution. The initial pH of the pregnant leach solution was checked by a pH meter as well as pH paper. Whenever liquid tannin was to be used for the precipitation of germanium, the calculated amount of solid tannin was dissolved in distilled water and added to the solution. At the end of each precipitation experiment, the precipitated solids were separated from the solution by filtration using a filter funnel and a suitable filter paper. Finally, the filtrates were analyzed for germanium and other metals by AAS. Percent precipitation of germanium and other metal values were calculated using the initial and final analysis of the solution.

The tannin used in the precipitation experiments was purchased from Sümer Holding located in Salihli. The tannin used was supplied as spray dried valonea extract having a minimum of 70% tannin.

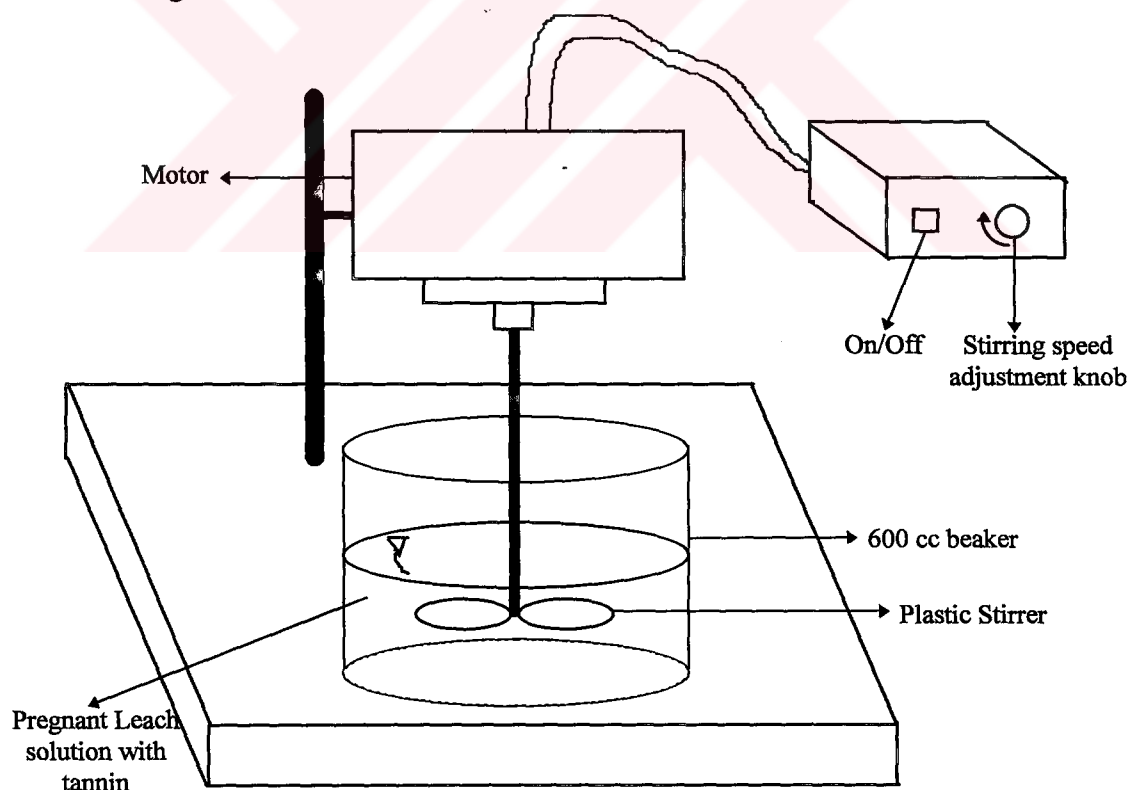


Figure 3.2. Set-up of Germanium Precipitation by Tannin Experiments

### 3.3. Characterization of Copper Cake of Çinkur

The copper cake obtained from Çinkur in the ground form was characterized physically, chemically and mineralogically. The results of characterization are summarized below:

#### 3.3.1. Physical Characterization

The specific gravity of the copper cake was measured to be 3.38 by an air pycnometer and its bulk density was 1.23 gram/cc. The dry screen analysis of the Çinkur copper cake in as received form is given in Table 3.1. As it can be seen from the table, about 84% of the ground sample was below 100 mesh (150 microns). The Çinkur copper cake was leached in this form without further grinding.

Table 3.1. Dry Screen Analysis of Copper Cake

Tyler Mesh	Wt.% Oversize	Cumulative Wt.% Oversize	Cumulative Wt.% undersize
48	1.95	1.95	98.05
65	1.13	3.08	96.92
100	12.79	15.37	84.13
150	18.37	34.74	65.26
200	37.37	72.11	27.89
270	12.86	84.97	15.03
-270	15.03	-	-
Σ	100.00		

### 3.3.2. Chemical Characterization

A representative sample of the copper cake was taken and ground before chemical analysis. Most of the chemical analysis of the copper cake were done by AAS except SiO<sub>2</sub> which was determined by the gravimetric analysis. The results were checked against those obtained from Çinkur. There was reasonable agreement between the chemical analysis of two different laboratories. The results of chemical analysis of the Çinkur copper cake are given in Table 3.2.

Table 3.2. Chemical Composition of Copper Cake

Ge (ppm)	Cu (%)	Zn(%)	Cd (%)	Ni (%)	Co (%)	Fe (%)	Pb (%)	As(%)	Sb (%)	SiO <sub>2</sub> (%)
700	15.33	15.63	1.66	1.33	0.64	0.35	2.62	12.6	0.18	3.42

### 3.3.3. Mineralogical Characterization

For the mineralogical characterization of the copper cake x-ray diffraction analysis, optical microscopy and scanning electron microscopy investigations were undertaken.

The x-ray diffraction analysis was performed by using the Regaku Geigerflex X-ray diffractometer. The X-ray diffraction pattern obtained indicated the presence of copper oxide (Cu<sub>2</sub>O), lead silicate (PbSiO<sub>3</sub>.xH<sub>2</sub>O), lead oxide (PbO and PbO<sub>2</sub>), lead oxysulphate (Pb<sub>3</sub>O<sub>2</sub>SO<sub>4</sub>), oxidized zinc containing arsenic and copper ((Zn,Cu)<sub>2</sub>(AsO<sub>4</sub>)OH), zinc oxysulphate (Zn<sub>3</sub>O(SO<sub>4</sub>)<sub>2</sub>), hydrated zinc sulphate

( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), hydrated zinc sulphite ( $\text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O}$ ) and copper arsenic sulphite ( $\text{Cu}_{24}\text{As}_{12}\text{S}_4$ ). The diffraction pattern of the copper cake with the peaks of the mentioned phases can be seen in Figure 3.3.

The mineralogical analysis using the Leitz-Orthoplan optical microscope indicated the presence of small amounts of mica (biotite), quartz ( $\text{SiO}_2$ ), limonite ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ), malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ), pyrite ( $\text{FeS}_2$ ), wustite ( $\text{FeO}$ ), metallic copper in addition to the above named minerals. Photographs in Figure 3.4-3.7 show the main constituents of the copper cake.

Scanning electron microscopy (SEM) analysis of the copper cake was done by the Jeol JSM-6400 model scanning electron microscope and EDS Tracor Series II Analysis System on specimens previously prepared for the optical microscopic investigation.

SEM analysis confirmed the findings of x-ray diffraction and optical microscopy studies. The metallic copper particles were oxidized on their surface. On the other hand, substantial numbers of oxide or sulphate phases containing copper, arsenic, zinc, nickel, cobalt and cadmium were found. The point analysis of these complex phases varied quite substantially from point to point. Lead was generally present in oxide or silicate form. Due to the scarcity of germanium, neither its presence nor its distribution among various phases could be determined. As shown in SEM element mapping of copper cake Figure 3.11 and 3.12. Refer to photographs in Figures 3.8-3.12 for the above mentioned observations. In conclusion, it can be said that the copper cake was mainly composed of oxidized metallic copper and oxidized complex metallic phases having Zn, Cu, As, Ni, Co, Cd in their

structure. The degree of oxidation was dependent on duration of storage of the cakes in the stock yard at Çinkur.

But to give an opinion, an example is given here for the distribution of germanium among various phases; A mineralogical study was carried out on the neutral leach residue and weak acid leach residue generated from Gordonsville zinc concentrate at the Clarksville Electrolytic Zinc Plant of Savage Zinc Inc. The intent was to characterize the mineral forms and associations of germanium. The major germanium carrier is the iron gel-silica gel phases, but the modest amounts of Ge are present in the ZnO, ZnFe<sub>2</sub>O<sub>4</sub>, sphalerite, and Zn-Fe-Pb silicate phases in the neutral leach residue. In the weak acid leach residue, the major Ge carrier is the iron gel-silica gel phases which contain up to 1.7 % Ge and accounts for ~ 70 % of the total Ge content of this residue. The remaining Ge is carried by the Zn-Fe-Pb silicate, ZnFe<sub>2</sub>O<sub>4</sub>, and some of the rare Mn-Pb-Fe oxide phases [34].

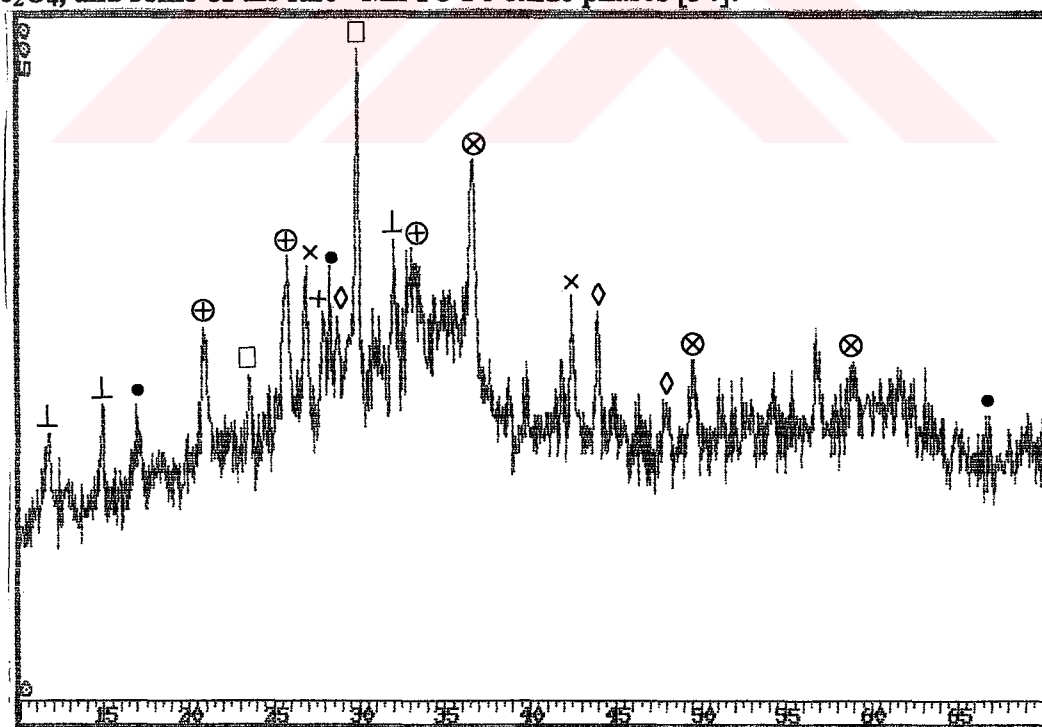


Figure 3.3. X-Ray Diffraction Pattern of Copper Cake : ×; Cu<sub>2</sub>O, ●; PbO, +; Pb<sub>3</sub>O<sub>2</sub>SO<sub>4</sub>, ◇; PbO<sub>2</sub>, □; (ZnCu)<sub>2</sub>(AsO<sub>4</sub>)(OH), ⊗; Cu<sub>24</sub>As<sub>12</sub>S<sub>31</sub>, ⊕; ZnSO<sub>4</sub>.7H<sub>2</sub>O, ⊥; ZnSO<sub>3</sub>.2.5 H<sub>2</sub>O

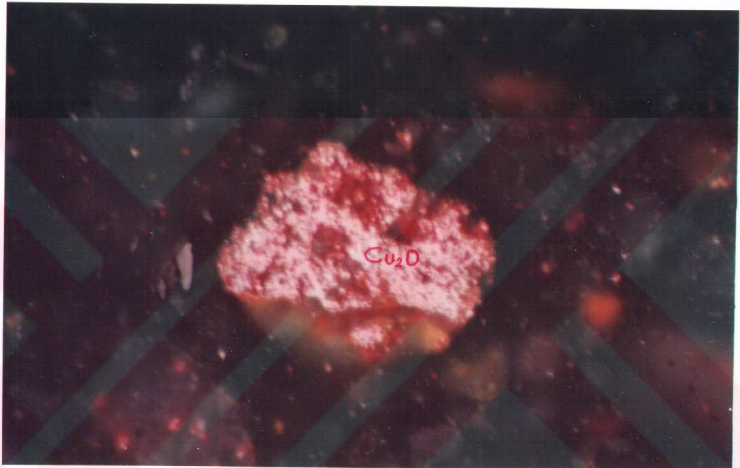


Figure 3.4. Optical Microscope Photograph of Copper Cake : Cuprite.

(320X)

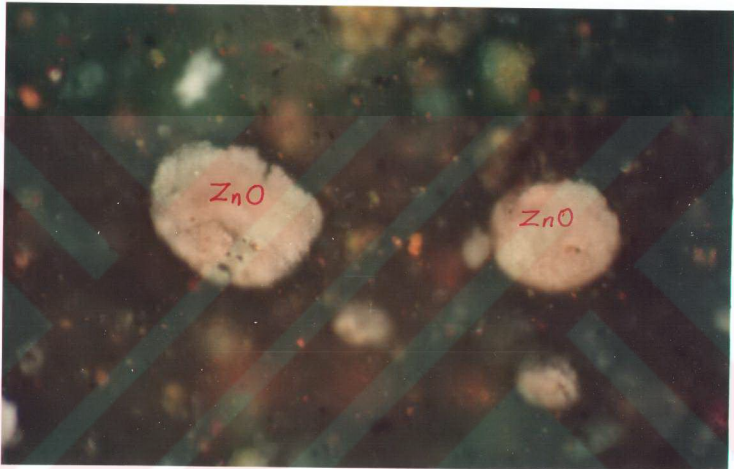


Figure 3.5. Optical Microscope Photograph of Copper Cake : Zincite.

(320X)



Figure 3.6. Optical Microscope Photograph of Copper Cake: Pyrite and Wustite.  
(320X)



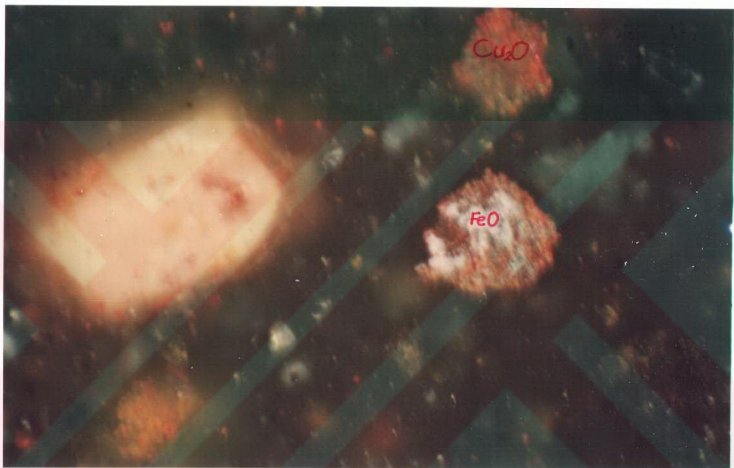


Figure 3.7. Optical Microscope Photograph of Copper Cake : Wustite and Cuprite.  
(320X)

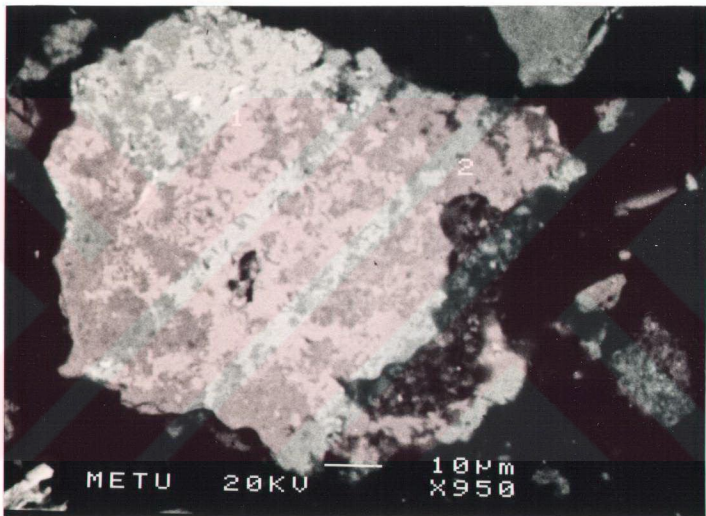


Figure 3.8. SEM Photograph of Copper Cake : Elemental Analysis of Point 1;  
94.57 Wt. % Cu, 5.43 Wt. % As, Elemental Analysis of Point 2;  
37.62 Wt.% Cu, 28.15 Wt. % Zn, 17.21 Wt.% As, 7.31 Wt.% S,  
3.23 Wt.% Si, 6.18 Wt.% Cd .

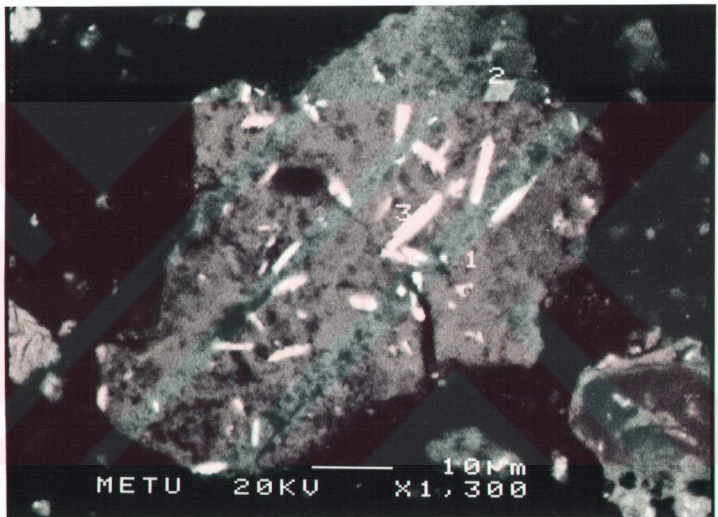


Figure 3.9. SEM Photograph of Copper Cake : Elemental Analysis of Point 1; 31.86 Wt. % Cu, 17.00 Wt. % Zn, 7.10 Wt. % Cd, 30.77 Wt. % As, 1.23 Wt. % Co, 1.66 Wt. % Ni, 6.93 Wt. % S, 3.43 Wt. % Si, Elemental Analysis of Point 2; 27.91 Wt. % Zn, 57.29 Wt. % Fe, 4.81 Wt. % Cu, 2.56 Wt. % Si, 5.32 Wt.%As, 2.11 Wt. % Mn, Elemental Analysis of Point 3; 5.36 Wt. % Si, 3.71 Wt. % Cu 1.28 Wt. % Zn, 89.65 Wt. % Pb.

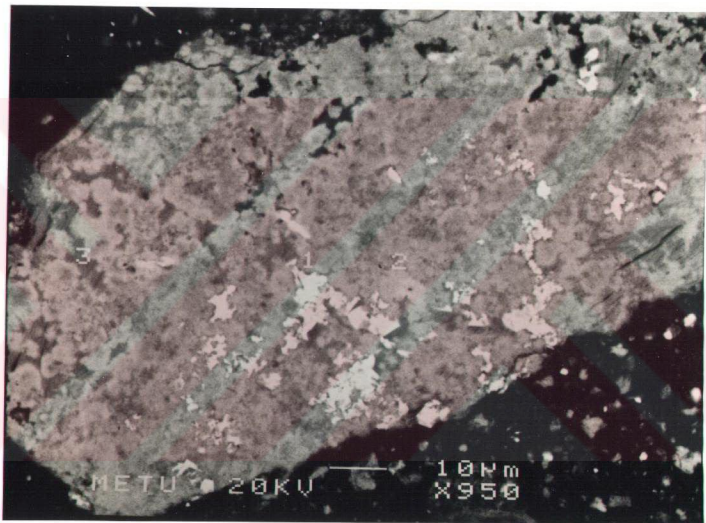


Figure 3.10. SEM Photograph of Copper Cake : Elemental Analysis of Point 1; ~ 100 Wt. % Cu, Elemental Analysis of Point 2; 27.89 Wt. % Cu, 21.05 Wt. % Zn, 1.33 Wt. % Cd, 43.10 Wt. % As, 0.52 Wt. % Co, 1.14 Wt. % Ni, 1.17 Wt. % S, 3.79 Wt. % Si, Elemental Analysis of Point 3; 38.67 Wt. % Cu, 27.45 Wt. % Zn, 0.92 Wt. % Cd, 7.87 Wt. % As, 1.83 Wt. % Co, 6.17 Wt. % Ni, 15.32 Wt. % S, 1.77 Wt. % Si .

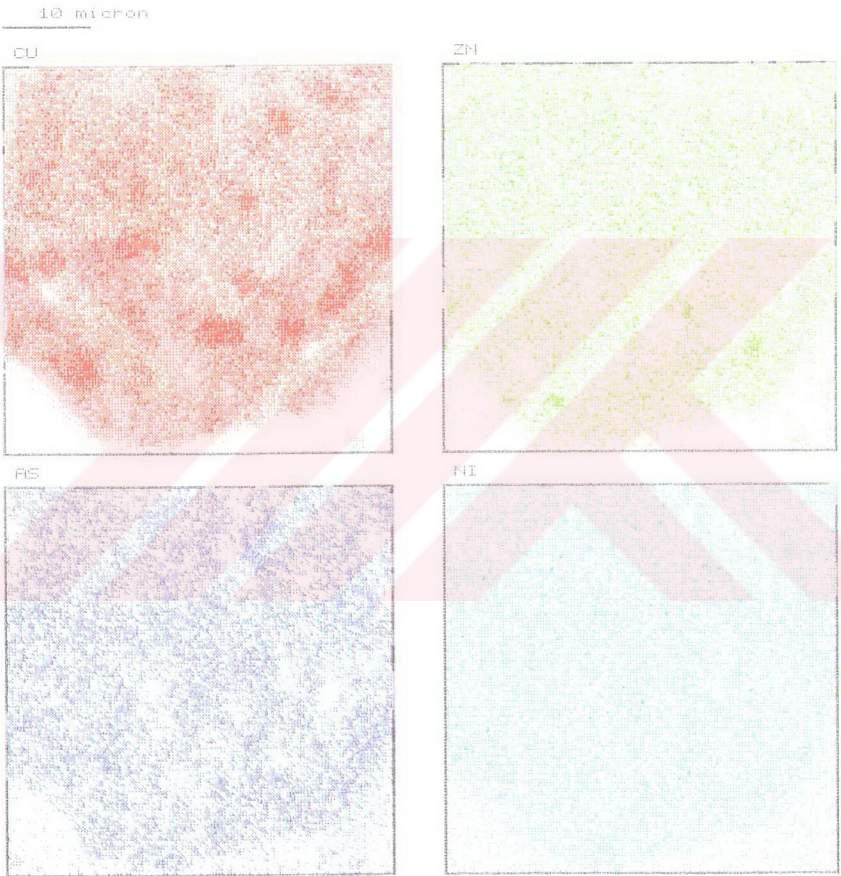


Figure 3.11. SEM Element Mapping of copper Cake

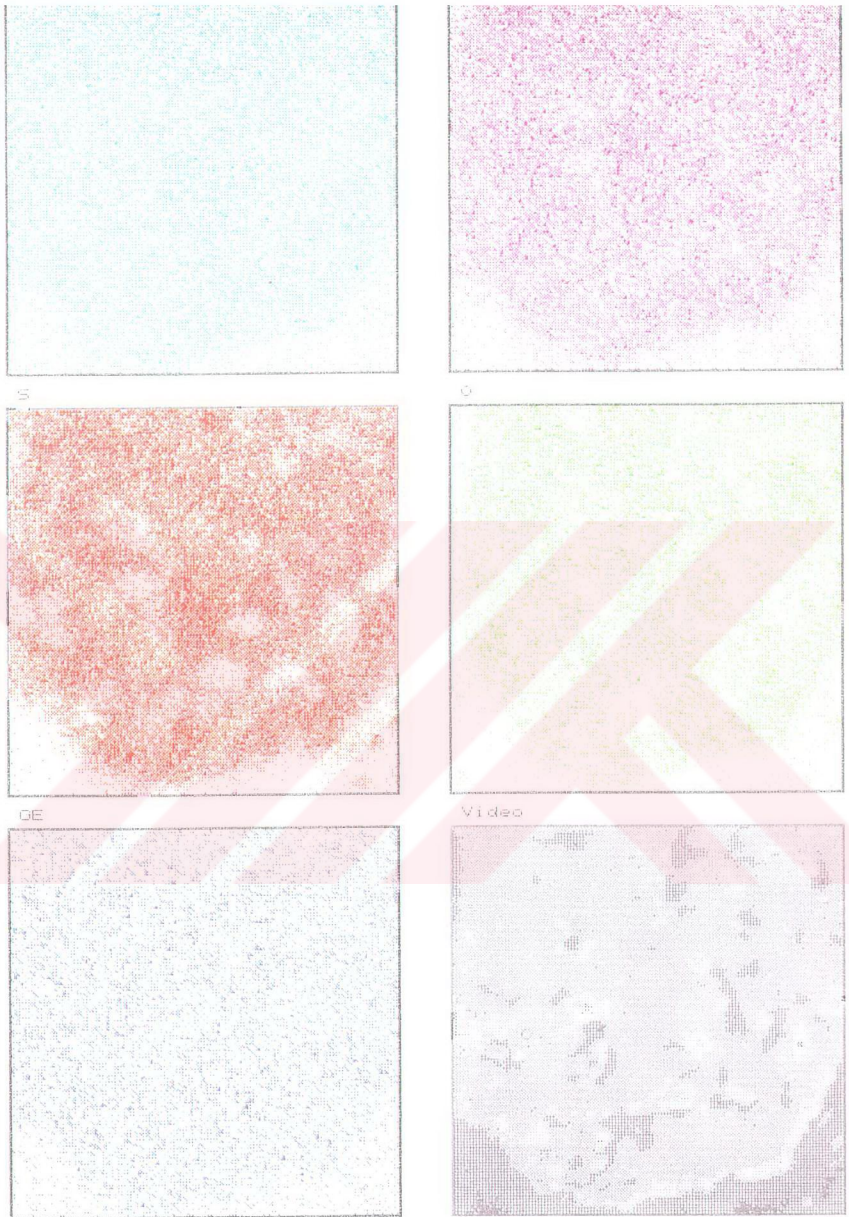


Figure 3.12. SEM Element Mapping of Copper Cake

### 3.4. Description of the Germanium Source of Çinkur Plant

In the literature germanium is known to be a detrimental impurity over the electrolysis of zinc because germanium reduces the hydrogen overpotential and also because it is more noble than zinc in the EMF series [35]. Çinkur zinc plant produces electrolytic zinc requiring the leach solution to be purified prior to electrolysis from the impurities such as, Ge, Tl, Cd, Cu, Co, Ni, etc. In connection with this, the residues from the solution purification section are the richest source of germanium at Çinkur. Figure 3.13 shows the production of the copper cake in Çinkur zinc plant. Previous germanium mass balance studies without the use of Iranian concentrate indicated that about 59% of the germanium came from the Turkish zinc ores and the remaining 41% of the germanium input originated from the coal used in the Waelz kiln. On the other hand, the mass balance indicated that about 50% of the germanium input was lost to the leach residue.

The losses of germanium to the Waelz slag accounted for about 30%. The germanium lost to the purification residues was only 16% of the total input [33].

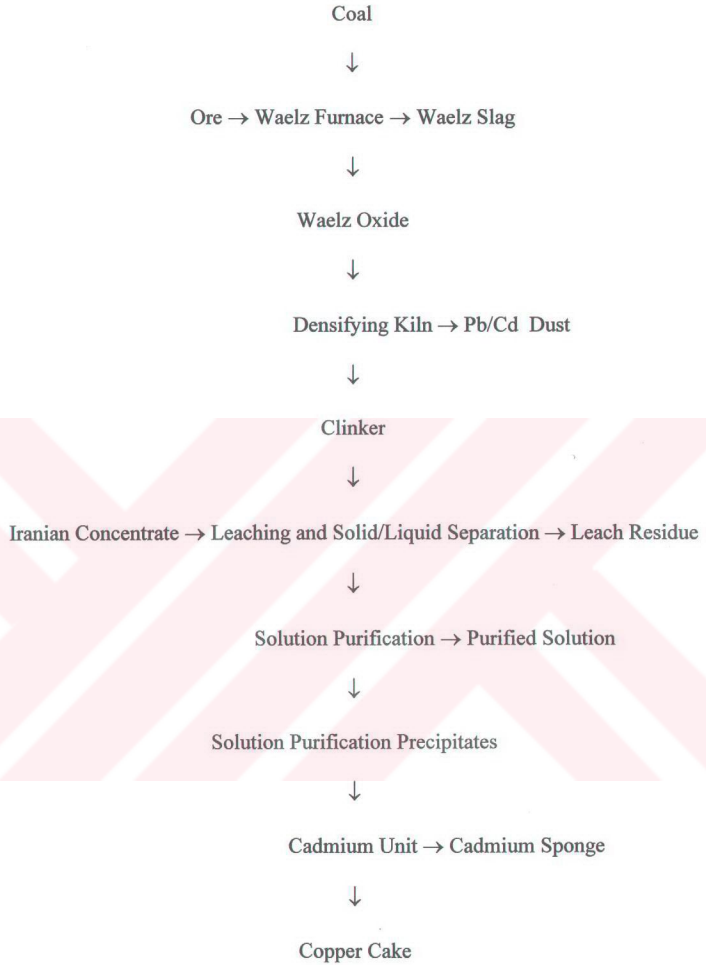


Figure 3.13. Production of Copper Cake in Çinkur



## CHAPTER 4

### RESULTS AND DISCUSSIONS

In this chapter, the results of leaching and tannin precipitation experiments are presented and discussed. First of all, the leaching behavior of copper cake was investigated in order to find out the optimum conditions of leaching. Later, the precipitation behavior of germanium from pregnant leach solution with tannin was investigated to determine the optimum conditions of precipitation. Also, in order to overcome solid-liquid separation problems after leaching a series of preliminary experiments were done by changing the experimental procedure used and the findings are reported.

#### 4.1. Leaching Experiments

Çinkur copper cake samples were treated with dilute sulphuric acid solution . The copper cake used in the leaching experiments was previously ground to 84% minus 100 mesh (150 microns). Throughout the leaching experiments duration of leaching, acid concentration, temperature of leaching, solid-liquid ratio and effect of addition of chemical oxidants have been examined in order to determine the technical optimum conditions (Table 4.1.). Stirring speed was kept constant in each test.

Table 4.1. Conditions of Copper Cake Leaching Experiments .

Exp.Code Number	Weight of Sample(g)	Leaching Temp.(°C)	Acid Conc (gpl)	S/L Ratio (g/cc.)	Leaching Duration(hr)	Air (l/min.)	MnO <sub>2</sub> (g)
L 1	50	85	0	1/4	3	-	-
L 2	50	85	150	1/4	3	-	-
L 3	50	85	150	1/4	2	-	-
L 4	50	85	150	1/4	1	-	-
L 5	50	85	150	1/4	1/2	-	-
L 6	50	85	75	1/4	1/2	-	-
L 7	50	85	100	1/4	1/2	-	-
L 8	50	85	150	1/4	1/2	-	-
L 9	50	40	150	1/4	1/2	-	-
L 10	50	60	150	1/4	1/2	-	-
L 11	50	85	150	1/4	1/2	-	-
L 12	25	85	150	1/8	1/2	-	-
L 13	50	85	150	1/4	1/2	-	-
L 14	100	85	150	1/2	1/2	-	-
L 15	50	85	150	1/4	1/2	1.43	-
L16	50	85	150	1/4	1/2	1.43	0.25

In the first leaching experiment, the leaching reagent was chosen to be water while the other variables were 85<sup>0</sup>C for leaching temperature, 3 hours for duration of leaching and ¼ for solid-liquid ratio. As given in Table 4.2, the leach recoveries of both germanium and the other metals were substantially low. This was thought to result from the negligible solubilities of the phases present in the samples in water. So in all the following leaching experiments, sulphuric acid was chosen as the leaching reagent.

Table 4.2. Results of Copper Cake Leaching Experiments.

Exp. Code Number	Weight of Leach Residue(g)	Leach Recoveries of Metals (%)						
		Ge	Cu	Zn	Cd	Ni	Fe	Co
L 1	39.73	2.3	4.1	14.3	34.2	30.4	3.1	45.9
L 2	9.54	75.4	95.6	98.9	98.9	99.7	88.8	99.5
L 3	9.80	75.8	94.6	99.3	99.0	99.6	84.6	99.3
L 4	10.00	76.7	94.7	98.9	98.8	99.5	88.9	99.5
L 5	10.33	78.5	93.8	99.0	98.5	99.4	86.0	99.5
L 6	21.27	49.3	49.7	86.3	78.2	95.8	18.0	98.7
L 7	13.34	72.8	83.3	97.4	82.7	99.3	55.6	99.7
L 8	10.34	78.4	93.6	99.9	99.9	99.9	89.8	99.9
L 9	10.54	81.9	93.4	99.0	97.2	88.3	84.8	85.2
L 10	10.95	75.4	93.9	99.0	98.7	99.8	88.6	99.7
L 11	10.00	78.4	93.6	99.4	98.9	99.4	85.7	99.3
L 12	4.27	92.7	99.1	99.9	99.9	99.6	99.3	99.9
L 13	10.10	78.6	93.7	99.2	98.5	99.5	84.9	99.4
L 14	44.94	23.4	42.8	86.8	87.1	93.9	24.9	94.2
L 15	9.75	83.4	99.23	99.1	98.6	99.8	82.0	99.9
L 16	9.76	81.0	99.0	99.8	98.6	99.7	80.7	99.7

#### 4.1.1. Effect of Duration of Leaching on the Leach Recoveries of Metal Values

The first set of experiments involved the examination of the effect of duration of leaching on the leach recoveries of metal values and they were coded as L2-L5. The experimental duration's were varied between 0.5 and 3 hours while the other parameters were kept constant as 150 gpl sulfuric acid concentration, 85<sup>0</sup>C leaching temperature and solid-liquid ratio of 1/4. As given in Table 4.2 and shown in Figures 4.1 and 4.2, about half an hour duration of leaching was sufficient for the optimum dissolution of each metal value including germanium. However, the leach recovery of

germanium was about 78% which was lower than those of Ni, Co, Cd, Zn and Cu. So, it can be concluded that the leaching duration of the copper cake is quite short and it can even be made shorter by decreasing the particle size of the cake by further grinding.

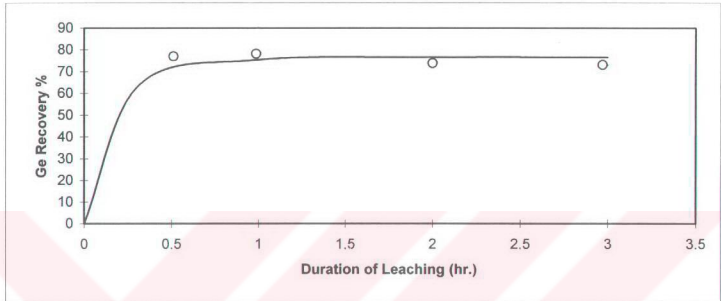


Figure 4.1. Effect of Duration of Leaching on the Leach Recovery of Germanium

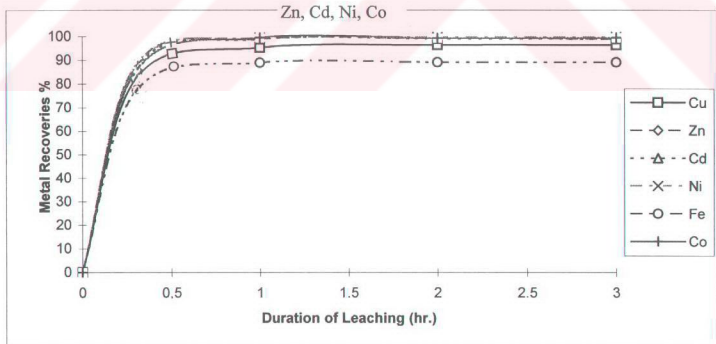


Figure 4.2. Effect of Duration of Leaching on the Leach recoveries of Other Metal Values.

#### 4.1.2. Effect of Acid Concentration on the Leach Recoveries of Metal Values

The second group of experiments were carried out by keeping constant the solid-liquid ratio at 1/4, the leaching duration at half an hour and the temperature at 85<sup>0</sup>C while changing acid concentration between 75 and 150 gpl H<sub>2</sub>SO<sub>4</sub>. The results which were obtained from these experiments coded L6-L8 are given in Table 4.2 and plotted in Figures 4.3 and 4.4. As it can be seen from the figures, the leach recoveries of germanium as well as other valuable metals like copper, nickel, cobalt, zinc, and cadmium increased with increasing acid concentration. This was due to the faster dissolution of oxidized phases that were present the copper cake at higher acid concentrations. Examination of the mentioned figures indicated that when the acid concentration was chosen as 150 gpl H<sub>2</sub>SO<sub>4</sub>, about 78% of the germanium present in the copper cake could be taken into solution. The leach recoveries of all the other valuable metals were close to 99%. Only the dissolution's of arsenic and iron present in the cake were not complete. For acid concentrations of 75, 100 and 150 gpl the amount of arsenic leached varied as 4.0, 13.3 and 23.3%, respectively. Acid concentrations beyond 150 gpl were not tried since it is reported in the literature that at higher acid concentration dissolved germanium starts to precipitate out from the solution resulting in lower leach recoveries[36].

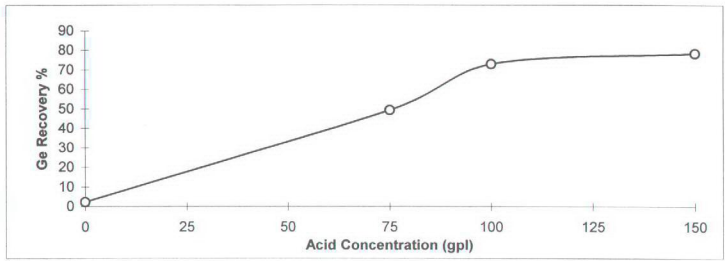


Figure 4.3. Effect of Sulphuric Acid Concentration on the Leach Recoveries of Germanium.

So, 150 gpl sulphuric acid concentration was decided to be the optimum because the highest leach recoveries could be attained by using this concentration and also because of the fact that Çinkur spent acid contains the same amount of acid . Industrially, the spent acid can easily be used for leaching of the cake instead of purchased sulphuric acid.

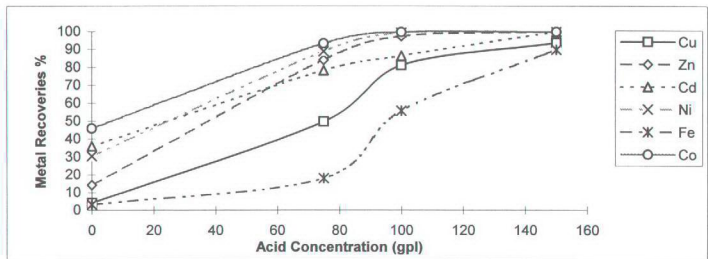


Figure 4.4 Effect of Sulphuric Acid Concentration on the Leach Recoveries of Other Metal Values .

#### **4.1.3. Effect of Temperature on the Leach Recoveries of Metal Values**

The following third series of experiments were carried by varying the leaching temperature in the range of 40 and 85<sup>0</sup>C. Throughout these experiments, the other leach parameters were kept constant at 150 gpl H<sub>2</sub>SO<sub>4</sub> concentration, half an hour duration of leaching and at a solid-liquid ratio of ¼. The code numbers of these experiments were L9-L11. All the obtained data are summarized in Table 4.2 and presented in graphical form in Figures 4.5 and 4.6. As it can be seen from Figure 4.5 that the germanium leach recovery was not too much affected by changing leach temperature in the experimental range studied. However, some valuable metals like cadmium, zinc and copper behaved in a similar manner to germanium on the other hand the leach recoveries of cobalt and nickel increased with increasing leaching temperature especially in the range of 40 to 60<sup>0</sup>C. So, by keeping the leaching temperature low the dissolution of cobalt and nickel could be controlled to a limited extend. If selective leaching is not the aim, the temperature of leaching could be controlled between 60 to 85<sup>0</sup>C. At temperatures beyond 85<sup>0</sup>C, evaporation losses from the leach tank would be excessive so it should be avoided.

#### **4.1.4. Effect of Solid-Liquid Ratio on the Leach Recoveries of Metal Values**

Experiments of the fourth group were made to examine the effect of solid-liquid ratio over the leach recoveries of germanium and the other valuable metals present in the copper cake. These experiments coded as L12-L14 were carried out at

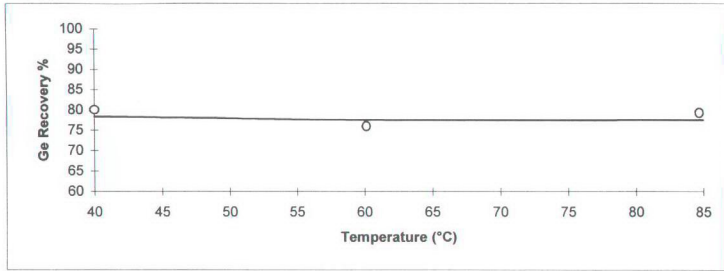


Figure 4.5. Effect of Temperature on the Leach Recovery of Germanium

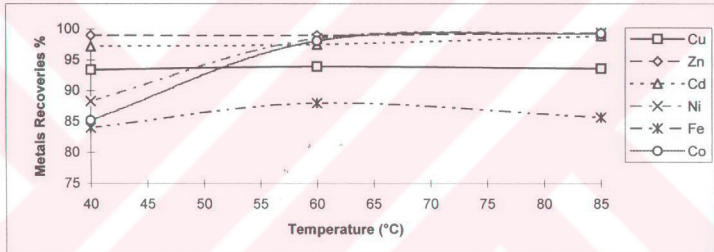


Figure 4.6. Effect of Temperature on the Leach Recovery of Other Metal Values .

solid-liquid ratio changing from 1/2 to 1/8 while the other parameters were kept constant as 150 gpl sulphuric acid concentration, 85<sup>0</sup>C of leaching temperature and half and hour for the leaching duration. The results obtained are given in Table 4.2 and Figures 4.7 and 4.8. By looking at the Figures 4.7 and 4.8, it was decided that a solid-liquid ratio of 1/4 could be the best choice available because an increase in the amount of solids in the leach system decreased the leach recoveries sharply, while a



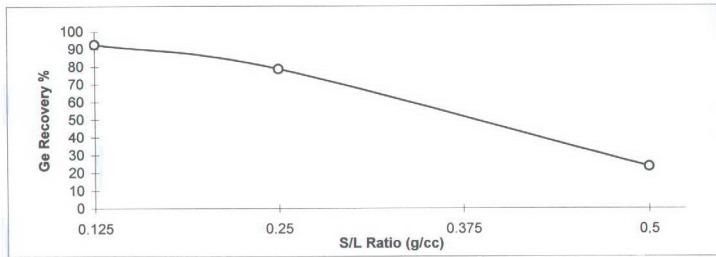


Figure 4.7. Effect of Solid-Liquid Ratio on the Leach Recovery of Germanium .

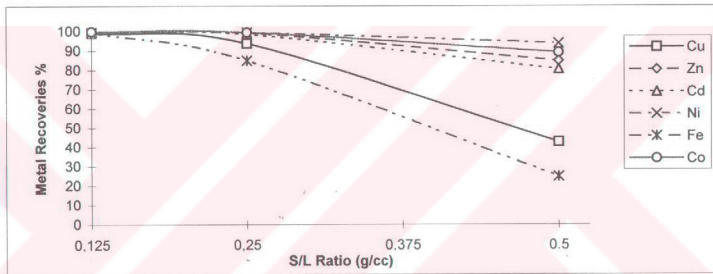


Figure 4.8. Effect of Solid-Liquid Ratio on the Leach Recovery of Other Metal Values

drop in percent solids was not generally economical industrially. The higher leach recoveries of metals with decreasing percent solids was thought to be due to the higher chance of solid particles to get in contact with the leach reagent when the percent solids was low. There was also an decrease in the amount of arsenic leached with increasing solid content in the pulp. In the experiments coded L12, 13 and 14, the amounts of arsenic that passed into solution were 29.1, 23.0 and 1.5%, respectively.

#### **4.1.5. Effect of Chemical Oxidant and Air on the Leach Recoveries of Metal Values**

The last three experiments of leaching were carried out in order to find out the effect of addition of a chemical oxidant like  $MnO_2$  and air on the leach recoveries of valuable metals. Manganese dioxide was added in the form of a pure solid power and the air was pumped into the leach solution by means of an air pump. The constant conditions of leaching were as follows: Leaching temperature  $85^{\circ}C$ , acid concentration 150 gpl, duration 1/2 hr and solid-liquid ratio of 1/4. The results of these experiments coded as L15 and 16 are also given in Table 4.2. As it can be seen from the mentioned table, the leach recoveries of germanium and copper increased and that of iron decreased with the pumping of air into the leach solution. Air helps the oxidation and faster dissolution of copper cake. Since the copper cake was not fully oxidized during its storage out in the air, the pumping of air resulted in the increased oxidation of especially unoxidized phases present in the cake. The decrease in iron leached was most probably due to the oxidation and precipitation of iron in solution by oxygen present in air. In conclusion it can be said that the pumping of air to the leach solution will increase the rate as well as the recovery of germanium and copper from the copper cake.

#### **4.1.6. Preliminary Studies in order to Overcome Leach Solution Filtration Problems**

Due to the formation of silica gel during the leaching of copper cake, the solid-liquid separation was found to be difficult after the completion of leaching

operation. In order to overcome this problem various leaching procedures were tried in order to minimize the difficulty. The aim was to minimize or avoid the formation of silica gel by following the most suitable leaching procedure. For this purpose, the three different leaching procedures tried were as follows :

1. The copper cake was added to 184cc of distilled water at room temperature. Then, 16cc of sulphuric acid was added and the mixture was heated to 85°C while stirring magnetically for the leaching purposes.

2. The distilled water of 184cc volume was initially heated to 85°C and then the copper cake was added into this water while stirring. Later, 16cc of sulphuric acid was added and leached.

3. The distilled water of 184cc volume and 16cc of sulphuric acid were mixed at room temperature and then heated to 85°C. Finally, the copper cake was added to the heated dilute acid solution and leached.

In all of these leaching experiments, the acid concentration was chosen to be 150 gpl H<sub>2</sub>SO<sub>4</sub>, duration of leaching 1/2 hr, leaching temperature 85°C and solid-liquid ratio 1/4 . For a filtration duration of 45 minutes, the amounts of pregnant leach solution filtered were as follows: 16, 22 and 14cc, respectively. These preliminary filtration tests indicated that the best filtration rate could be obtained by using the second procedure given above. Apparently, the use of this procedure resulted in formation of limited amount of silica gel as compared to the others. In the

normal leaching experiments described in the previous sections, the third procedure was used in order to time the leaching experiments more accurately.

#### **4.2. Tannin Precipitation Experiments**

As mentioned before, the use of tannin for the recovery of germanium from pregnant leach solutions containing low concentrations of germanium (i.e. less than 1gpl ) by precipitation has been a widely used technique in the industry for a long time. Since, the Çinkur pregnant leach solutions obtained by the leaching of copper cake, had less than 1000 ppm Ge for its precipitation tannin was preferred.

For the optimization of the tannin precipitation of germanium, the following parameters and factors were investigated: Amount of tannin addition, duration of precipitation, stirring speed, pH of pregnant leach solution, the effect of stagewise additions of tannin, the effect of the use of liquid tannin solution and the effect of air blowing into the solution.

For the precipitation experiments, a stock solution with a volume 15 liters was used. This stock solution was produced during the pilot plant leaching of copper cake at Çinkur. The chemical analysis of the stock solution was determined as:169 ppm Ge, 29.3 gpl Cu, 24.0 gpl Zn, 7 ppm Pb, 867 ppm Ni, 491 ppm Co, 4.6 gpl Cd, 4.2 gpl Fe and 3550 ppm As. The pH value of this solution was measured as 1.3.

Table 4.3. Results of Germanium Precipitation by Tannin.

Exp. Code Number	Volume of Leach soln.(cc)	Weight of Tannin (g.)	pH	Mass Tannin / Mass Ge	Duration of ppt. (hrs.)	Mixing Speed (rpm)	% Ge Precipitation
P 1	250	0.8500	1.3	20	2	820	67.7
P 2	250	1.0625	1.3	25	2	820	73.1
P 3	250	1.2750	1.3	30	2	820	89.2
P 4	250	1.4875	1.3	35	2	820	94.0
P 5	250	1.2750	1.3	30	½	820	83.6
P 6	250	1.2750	1.3	30	1	820	89.0
P 7	250	1.2750	1.3	30	2	820	90.6
P 8	250	1.2750	1.3	30	3	820	91.0
P 9	250	1.4875	1.3	35	1	700	80.0
P 10	250	1.4875	1.3	35	1	745	85.0
P 11	250	1.4875	1.3	35	1	820	90.0
P 12	250	1.4875	1.3	35	1	1070	92.0
P 13	250	1.4875	1.3	35	1	1335	92.0
P 14	250	1.1872	0.0	35	1	820	96.0
P 15	250	1.3626	0.5	35	1	820	95.0
P 16	250	1.4543	1.0	35	1	820	93.0
P 17	200	0.7308	1.5	35	1	820	70.0
P 18	249	1.1638	2.0	35	1	820	-
P 19	250	0.8500	1.3	20	1	820	72.0
P 20	250	1.0625	1.3	25	1	820	85.0
P 21	250	1.2750	1.3	30	1	820	90.0
P 22	250	1.4875	1.3	35	1	820	97.0
P 23	250	0.3400	1.3	8	1	820	27.0
P 24	250	0.2952	1.3	12	1	820	64.1
P 25	100	0.0971	1.3	16	1	820	82
P 26	250	1.4875	1.3	35	1	820	91.0
P 27	250	1.4875	1.3	35	1	820	89.4

The results of the precipitation experiments all of which carried out at room temperature are summarized in Table 4.3 with the experimental conditions used. The germanium recovery percentages have been calculated and reported with respect to

the difference between the germanium concentration in the pregnant leach solution stock and that remaining after the tannin precipitation.

#### **4.2.1. Effect of the Amount of Solid Tannin Addition on the Germanium Recovery**

In the first series of germanium precipitation experiments by the use of tannin, the effect of the amount of tannin addition was investigated. In these experiments, the amount of solid tannin addition was varied between 20 to 35 times the mass of germanium in solution. The increases were in step of 5 times the mass of germanium in solution and the experiments were coded as P1-P4. In all of these experiments the other variables were kept constant as follows: Precipitation at room temperature, pH of the pregnant leach solution 1.3, duration of tannin precipitation 2 hours, mechanical stirrer speed 820 rpm. The results of these experiments are given in Table 4.3 and Figure 4.9.

As it can be seen from the mentioned table and the figure, with the increasing amount of tannin addition there was an increase in the amount of germanium precipitated. With the tannin addition of 35 times the mass of germanium in solution, the recovery of germanium reached a maximum of 94%.

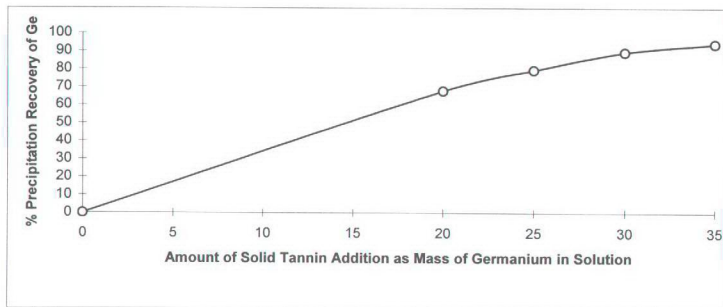


Figure 4.9. Effect of Amount of Solid Tannin Addition on the Percent Precipitation of Germanium .

#### 4.2.2. Effect of Tannin Precipitation Duration on the Germanium Recovery

The second group of experiments for the precipitation of germanium by tannin have been carried out at room temperature by keeping constant the following variables: 30 times the amount of germanium in solution as the amount of tannin addition, 820 rpm as the stirring speed, 1.3 as the pregnant solution pH while varying the duration of germanium precipitation between 0.5-3 hours. These experiments were coded as P5-P8 and the data obtained were also included in Table 4.3 and plotted in Figure 4.10.

From Table 4.3 and Figure 4.10, it can be seen that under the constant conditions specified above the germanium recovery by tannin precipitation increased only from 89% to 91% as the duration of precipitation increased from 1 hour to 3 hours.

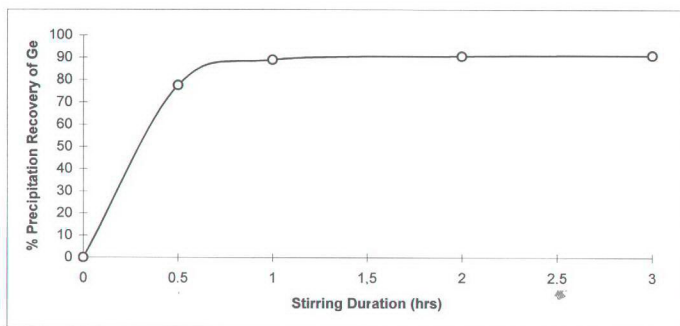


Figure 4.10. Effect of Stirring Duration on the Percent Precipitation of Germanium.

#### 4.2.3. Effect of Stirring Speed on the Precipitation of Germanium by Tannin

The next set of experiments were carried out in order to find out the effect of mechanical stirring speed on the recovery of germanium by tannin precipitation. In these room temperature experiments the amount of tannin added was kept constant at 35 times the amount of germanium in solution, the duration of precipitation was chosen to be 1 hour and the pH of the solution was again 1.3. The stirring speed of the mechanical stirrer was varied in the range of 700 to 1335 and measured by means of a stroboscope. The results obtained at different stirring speeds are summarized in Table 4.3 and Figure 4.11.

The analysis of the results as well as the figure showed the importance of the speed of stirring. The percentage of germanium precipitation increased with the increasing stirring speed. This increase was more substantial up to 820 rpm there



after it became slower. In industrial scale operations stirring speed becomes more important due the formation of froth which prevents the mixing of the tannin with the pregnant leach solution. Since tannin is a light material it tends to float at the surface of the solution. For the experimental conditions used in the laboratory, a stirring speed beyond 820 rpm would be desirable.

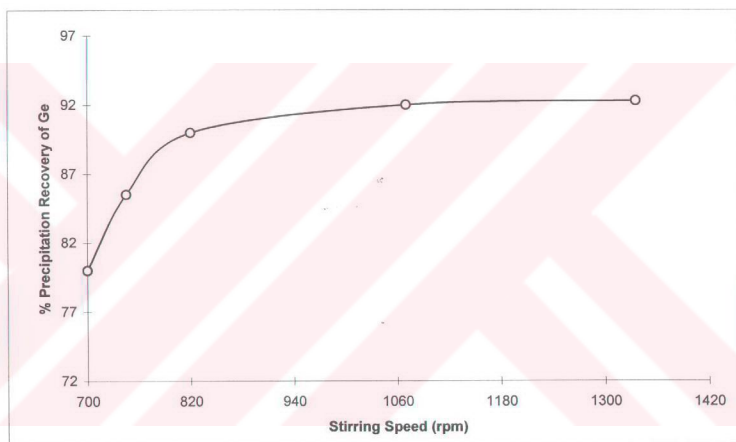


Figure 4.11. Effect of Stirring Speed on the Percent Precipitation of Germanium

#### **4.2.4. Effect of pH Values of Solution on the Precipitation of Germanium by Tannin**

The experiments of the fourth group involved the effect of initial pH value of the pregnant leach solution on the precipitation of germanium by tannin addition. These experiments coded as P14-P18 were carried out at pH of solution varying from 0 to 2.0 while the other parameters were kept constant as 1 hour stirring duration, 820 rpm as the stirring speed, 35 times the amount of germanium in solution as the tannin addition at room temperature. The results obtained are given in Table 4.3 and Figure 4.12. From the mentioned table and the figure, it is clear that the precipitation recovery of germanium dropped from 96% to 90% as the initial pH increased from 0 to 1.3 (original pH of the pregnant leach solution). About 71% of the arsenic in solution also precipitated with the tannin addition at a pH of 0.5. As the initial pH was tried to be increased beyond 1.3, the precipitation of solids high in arsenic was observed. This precipitation was accompanied with the loss of germanium to the precipitated solids. In these experiments, the pH adjustments were made by using concentrated sulphuric acid and ammonia solution.

In conclusion, it can be said that the initial pH of the pregnant leach solution should be left at its original value or lowered slightly by sulphuric acid addition.

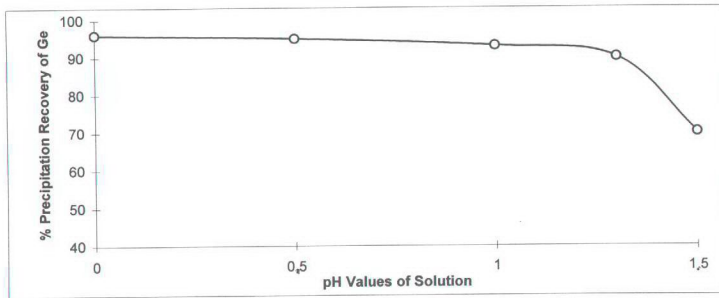


Figure 4.12. Effect of Pregnant Leach Solution pH on the Percent Precipitation of Germanium.

#### 4.2.5. Effect of the Amount of Tannin Solution Addition on the Precipitation of Germanium

The fifth series of experiments were made by using liquid tannin solution as the precipitant. The tannin solution was prepared by dissolving 10 grams of solid tannin in 100 cc of distilled water. The aim was to accelerate the precipitation rate of germanium by liquid-liquid contact. As in the case of the addition of solid tannin, the amount of tannin added as a solution was varied in the range of 20 to 35 times the amount of germanium present in pregnant leach solution. During these room temperature precipitation experiments, the other parameters were kept constant as 1 hour precipitation duration, 820 rpm stirring speed, 1.3 pH of pregnant leach solution. The results of these experiments which were coded from P19-P22, are also included in Table 4.3 and presented in graphical form in Figure 4.13. As can be seen from the table and the figure, the amount of germanium precipitated increased with

the increasing amount of addition of liquid solution of tannin. The highest recovery of germanium of 97% was obtained for an addition of 35 times the amount germanium present in the pregnant leach solution. If compared to solid tannin addition results, it can be seen that the liquid tannin solution was more effective in the precipitation of the germanium in solution. It was found to be possible to precipitate the germanium in solution in a shorter time and more efficiently. On the other hand, filtration problems were experienced in solid-liquid separation after precipitation by liquid tannin. The precipitate formed was with a very fine particle size which blocked the pores of the filter paper very quickly. Therefore, filtration took a long time to achieve. So this was the disadvantage of liquid tannin solution addition for the precipitation of germanium.

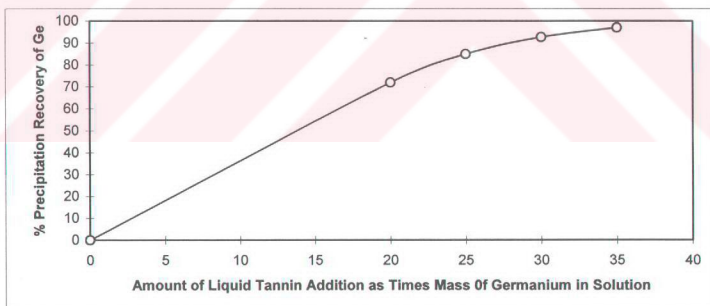


Figure 4.13. Effect of Amount of Liquid Tannin Addition on the Percent Precipitation of Germanium.

#### 4.2.6. Stepwise Solid Tannin Precipitation of Germanium

The next series experiments were made in order to investigate the effect of stagewise addition of solid tannin on the precipitation of germanium from the pregnant leach solution. At first, the amount of solid tannin added was 8 times the amount of germanium present in the pregnant leach solution. After precipitation, the solid precipitate was separated by filtration and the solution was analyzed again for the remaining germanium content. In the second stage of precipitation, the amount of solid tannin added was 12 times the amount of germanium remaining in the solution. After filtration and the separation of the precipitated solid, the solution was again analyzed in order to determine its germanium content as before. Finally, in the third stage the amount of solid tannin added to the solution was increased to 16 times the amount of germanium remaining in the solution. As before, after the filtration and separation of the germanium precipitate, the remaining germanium content of the solution was determined by AAS analysis and cumulative recovery of germanium was calculated. The results of these tests are given in Table 4.3 and Figure 4.14. In all of these room temperature experiments, the duration of precipitation was 1 hour in each stage, the stirring speed was kept constant at 820 rpm and no interstage additions were made for pH adjustment. As it can be seen from the mentioned table and the figure, the cumulative percentage of germanium precipitated after 3-stages of precipitation was 82% but the amount of total tannin used was the half of tannin used in normal germanium precipitation experiments. So a higher grade germanium precipitate was obtained with less tannin consumption. This has industrial importance.

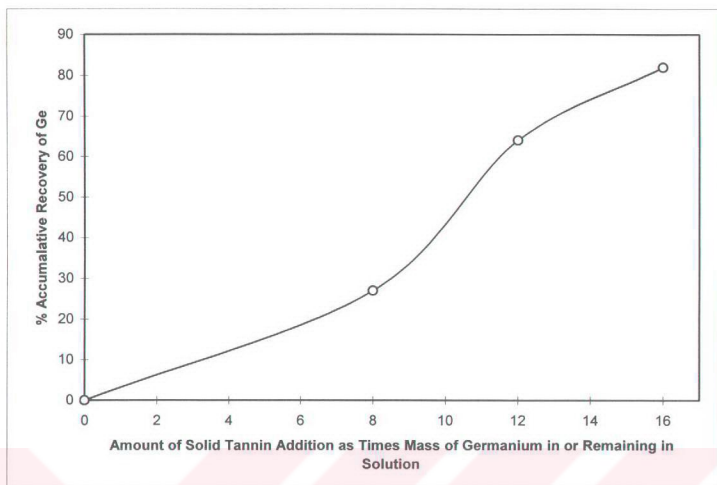


Figure 4.14. Effect of Stagewise Addition of Solid Tannin on the Percent Cumulative Precipitation of Germanium.

#### 4.2.7. Effect of Air Blowing into Solution on the Germanium Precipitation by Tannin

In the last two experiments coded as P26 and P27, the effect of pumping air into the pregnant leach solution during the precipitation of germanium by solid tannin addition was investigated. The results given in Table 4.3 indicated that the air blowing during germanium precipitation was not very effective in the acceleration of the rate of precipitation.

#### 4.2.8. Precipitation of Other Metals by Zinc Addition into Pregnant Leach Solution

The objective of these experiments was to precipitate the other metals like Cu, Co, Ni, Cd present in pregnant leach solution before germanium precipitation without precipitating the germanium. If this could be achieved, the tannin precipitation would then follow as the second stage. These experiments were carried out at room temperature but due to the exothermic reactions resulting on the addition of fine zinc powder to the solution, there was an increase in the temperature of precipitation. First of all, the stoichiometric amount of zinc powder necessary to precipitate the copper, nickel, cobalt and cadmium in pregnant leach solution was calculated and in the first experiment this amount was added. In the following experiments, the zinc powder added was increased by 25 and 50% over the stoichiometrically calculated amount. The results of these experiments are given in Table 4.4. As it can be seen from Table 4.4, the amount of copper precipitated increased with increasing addition of zinc powder.

Table 4.4. Effect of the Amount of Zinc Powder Addition on the Percent Precipitation of metals.

Exp.Code Number	Volume of Soln. (cc)	Amount of Zn (x stoichiometric Amount)	% Precipitation Recovery of Metals						
			Cu	Pb	Cd	Ni	Co	Fe	Ge
P 28	250	1.00	59.3	16.2	91.6	4.4	1.4	5.2	31.0
P 29	250	1.25	88.5	19.5	13.0	4.1	3.7	10.2	34.5
P 30	250	1.50	99.9	44.8	13.1	4.0	3.0	4.0	54.4

Unfortunately, some of the germanium in solution also precipitated with copper and the amount of germanium precipitated increased with increasing zinc powder additions. So selective precipitation of copper and germanium by zinc powder addition was found to be impossible. In conclusion, it can be said that it would be better to precipitate the germanium in pregnant leach solution first by tannin addition which could be followed with copper precipitation by zinc powder or steel scrap addition.



## CHAPTER 5

### CONCLUSIONS

The characterization of the copper cake or solution purification precipitate of Çinkur indicated that the ground cake was about 84% below 100 mesh. The chemical analysis of the cake showed that there was 700 ppm Ge, 15.33% Cu, 15.63% Zn, 1.66% Cd, 1.33% Ni, 0.64% Co, 0.35% Fe, 2.62% Pb, 12.62% As, 0.18% Sb and 3.42% SiO<sub>2</sub>. The mineralogical analysis using x-ray, optical microscope and scanning electron microscope indicated the presence of metallic as well as mostly oxidised complex type copper, zinc, arsenic, nickel, cobalt and cadmium containing phases. Due to the scarcity of germanium neither its presence nor its distribution among various phases could be determined.

The sulphuric acid leaching experiments were then optimized and the optimum conditions were determined as follows:

1. Leaching temperature range of 60 to 85<sup>0</sup>C.
2. 150 gpl sulphuric acid concentration.
3. Half an hour duration of leaching.
4. A solid to liquid ratio of 1/4

Air pumping into leach solution help the oxidation and faster dissolution of copper cake. Under the optimum conditions specified above the leach recovery of

germanium was 78%. The dissolution's of other metals like zinc, copper, nickel, cobalt, cadmium, etc. were almost complete.

After the optimization of leaching conditions of copper cake, the precipitation of germanium with tannin was optimized. The precipitation with tannin was preferred for the germanium recovery since the pregnant leach solution obtained after leaching had less than 1000 ppm Ge. The chemical analysis of the stock leach solution was determined as : 169 ppm Ge, 29.3 gpl Cu, 24.0 gpl Zn, 7 ppm Pb, 867 ppm Ni, 491 ppm Co, 4.6 gpl Cd, 4.2 gpl Fe and 3.5 gpl As. The pH value of this solution was measured as 1.3. The tannin precipitation experiments indicated that with the increasing amount of tannin addition there was an increase in the amount germanium precipitated. With the solid tannin addition of 35 times the mass of germanium in pregnant leach solution, the recovery of germanium by precipitation reached a maximum of 94%. As duration of mixing of tannin increased from 1 to 3 hours there was not a substantial change in the amount of germanium precipitated. So 1 hour was found to be long enough for the precipitation of the germanium from the pregnant leach solution. The stirring speed also effected the percentage of germanium precipitation and it is increased with the increasing stirring speed up to 820 rpm there after the increase becomes lower. So under the laboratory conditions, a stirring speed beyond 820 rpm would be desirable. On the other hand the experiments indicated that the initial pH of the pregnant leach solution should be left at its original value of 1.3 or lowered slightly by sulphuric acid addition for better germanium recovery using tannin precipitation. The addition of tannin in the form of solution was found to be more effective than the solid tannin addition but the precipitate formed was more difficult to separate from the solution. Finally, the addition of tannin in

stagewise manner was better than the single stage addition to the pregnant leach solution. By stagewise tannin addition, it was possible to decrease the tannin consumption as well as to increase the grade of the final germanium concentrate.

The experimental findings indicated that selective precipitation of copper and germanium with zinc powder was not possible. So, it was concluded that it would be better to precipitate the germanium first by tannin addition which could be followed with the precipitation of copper by zinc powder or steel scrap. As the final step the precipitation of zinc in the solution or recovery by electrowinning could be done.

The various experiments carried out during the course of this thesis showed that the germanium in the copper cake of Çinkur could be recovered without any difficulty. The alternative recovery technique for the germanium in the pregnant leach solution is solvent extraction. In the future this alternative should be investigated in detail. Also, the possibilities of production of pure germanium dioxide and germanium metal from the germanium concentrate obtained are to be investigated.

## REFERENCES

- [1] Glockling F., *The Chemistry of Germanium*, Academic Press, London & New York, 1969.
- [2] Jacobson D.M., *Special Features of Germanium and Gallium Supply and Demand*, Int. Journal of Mineral Processing, pp.C 45-49, 1987.
- [3] Adams J.H., *Features of Germanium*, Eng. Min. J., pp. 178-181, 1977.
- [4] Litchfield J.W., Watts R.L., Gurwell W.E., *A Methodology for Identifying Materials Constrains to Implementation of Solar Energy Technologies*, Pacific Northwest Laboratory, 1987.
- [5] Piedmont J.R. Riordon R.J., *The Supply of Germanium for Future World Demands*, Fourth European Electron-Optics Conference, 1988.
- [6] Adams J.H., Othmer K., *Germanium and Germanium Compounds*, Encyclopedia of Chemical Technology, Vol. 11, pp. 791-802.
- [7] Senke E., *Germanium*, U.S. Department of the Interior, Annual Review, 1994.
- [8] Shaskov Yu. M., *The Metallurgy of Semiconductors*, Consultants Bureau (English Translation), 1961.
- [9] Pilkington E.S., *Improvements in and Relating to the Extraction of Germanium*, Commonwealth of Australia Patent Specification 235803, 1959.
- [10] Anon, *What Lies Ahead of Germanium*, Eng. Min. J., Vol. 5, pp. 75-88, 1956.

- [11] Lebleu A., Fossi P., *Process for the Recovery and Purification of Germanium from Zinc Ores*, U.S. Pat. 4.090, 871, 1978.
- [12] Thompson A.P. and Musgrave J.R., *Germanium Produced As a Byproduct Has Become of Primary Importance*, *J. of Metals*, Vol. 4, pp. 1132-1137, 1952.
- [13] Harner H.R., *Germanium*, *Rare Metals Handbook*, Edited by Hampel C.A. pp. 188-197, 1961.
- [14] Mc Quiston F.W., Bechaud L.J., Allen C.B. and Young R.A., *What Lies Ahead for Germanium*, *Eng. and Min. J.*, Vol.157, pp.75-88, 1956.
- [15] Ratledge J.P., Ong J.N. and Boyce J.H., *Development of Metallurgical Practice at Tsumeb*, *Mining Eng.*, pp. 374-382, 1955.
- [16] Davydov V., *Germanium*, Gordon and Breach Science Publishers, , pp. 1-71, 1966.
- [17] Lebadeff, Y.E., Metuchen N.J. and Wetherill W.H., *Removal of Germanium Values from Copper Bearing Materials Containing Same*, U.S. Patent 2889196, 1959.
- [18] Andrianov A.M. and Poladyan V., *Separation and Concentration of Germanium from Solutions*, *Ind. Lab (USSR)* Vol. 40, p. 1268, 1974.
- [19] Wardell M.P. and Davidson C.F., *Acid Leaching Extraction of Gallium and Germanium*, *J. of Metals*, pp. 39-41, 1987.
- [20] Fishman M.A. and Sobelev D.S., *Practicing in the Benefication of Ores of Nonferrous and Rare Metals*, *Metallurgist*, pp. 27-42, 1959.
- [21] Shubov L. Ya., *Part 1, Benefication of Polymetallic Ores*, *Prob. Sov. Metallurgy*, Vol. 2, pp.46-62, 1957.

- [22] Rotledge J.P., Ong J.N. and Boyce J.H., *Production of Germanium*, Ming. Eng., Vol.7, pp.374-382, 1954.
- [23] Residue Processing at Portesula, Report, 1989.
- [24] O'Connor T.A., *Germanium's Electronic Upsurge*, Chem. Eng., Vol 4., pp.158-160, 1952.
- [25] Seifullina I.I, Pozharitskii A.F., Skrylev L.D., Belousova E. and Chistov A.S., *Isolation of Germanium Tannate and Gallate Complexes by the Flotation Method*, Zhurnal Prikladnai Khimii (English Translation: J. Applied Chemistry, USSR), Vol. 39, pp. 2077-2079, 1973.
- [26] Zelikman A.N., *Metallurgy of Rare Metals*, Israel Program for Scientific Translations, pp. 308-321, 1966.
- [27] Hoffmann J.E., *Advances in the Extractive Metallurgy of Selected Rare and Precious Metals*, J. of Metals, pp. 18-23, 1991.
- [28] Mayer Jim, Eagle-Picher, Industries Inc., Private Communication, 1996.
- [29] Cote G. and Bauer ., *Liquid-Liquid Extraction of Germaium with Oxine Derivatives*, Hydrometallurgy, pp.149-160,1980.
- [30] Zhou T., Zhong X. and Zheng L., *Recovering In, Ge and Ga from Zinc Residues*, Journal of Metals, pp. 36-40, 1989.
- [31] Matis K.A., Stalidis G.A. and Zoumbalis A.J., *Flotation of Germanium from Dilute Solutions*, Separation Science and Technology, Vol. 23, 347-362, 1988.
- [32] Hoffmann J.E., *Extracting and Refining Germanium*, J. of Metals, Vol. 39, pp. 42-45, 1987.
- [33] Akkurt S., *Recovery of Germanium and Other Metal Values from the Solution Purification Precipitates of Çinkur Zinc Plant*, M.S. Thesis, METU, 1991.

- [34] Dutrizac J.E., Chen T.T. and Longton R.J., *The Mineralogical Department of Germanium in the Clarksville Electrolytic Zinc Plant of Savage Zinc Inc.*, Metallurgical and Materials Transactions B, Vol. 27B, pp. 567-576, 1996.
- [35] Fukubayashi H.H., *Effect of Impurities and Additives on the Electrowinning of Zinc*, USBM, RI 7966, 1974.
- [36] Harbuck D.D., Morrison J.W. and Davidson C.F., *Optimization of Gallium and Ge Extraction from Hydrometallurgical Zinc Residues*, Light Metals, Edited by Campbell P.G., 1989.