REMOVAL OF COBALT FROM ZINC SULFATE SOLUTION BY CEMENTATION PRIOR TO ZINC ELECTROWINNING

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

BY

PINAR BURCU KAYIN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
IN
THE DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING

AUGUST 2003

Approval of the Graduate School of Natural and Applied Sciences.

Prof. Dr. Canan Özgen
Director

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

Prof.Dr. Bilgehan Ögel
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 in Metallurgical and Materials Engineering.

Prof. Dr. Yavuz A. Topkaya
Supervisor

Examining Committee Members:

Prof. Dr. Yavuz A. Topkaya

Prof Dr. Ahmet Geveci

Prof. Dr. İshak Karakaya

Assoc. Prof. Dr. Kadri Aydınol

Dr. Abdi Aydoğdu

ABSTRACT

REMOVAL OF COBALT FROM ZINC SULFATE SOLUTION BY CEMENTATION PRIOR TO ZINC ELECTROWINNING

Kayın, Pınar Burcu
M.S., Department of Metallurgical and Materials Engineering
Supervisor: Prof.Dr. Yavuz A. Topkaya

August 2003, 94 pages

The aim of this study was to investigate the removal of cobalt from zinc sulfate solution by cementation with the help of conventional and new type of additives that were 4% Sn-zinc alloy powder and 10% Sn-zinc alloy powder, respectively. Synthetic leach solutions containing 150 g/l Zn and 75 mg/l Co were prepared and used in all of the experiments. The parameters researched with the conventional method were the amount of arsenic trioxide and the effect of copper sulfate on cementation of cobalt. While using the alloys, the parameters studied were the amounts of arsenic trioxide, copper sulfate and tin containing zinc alloy powder additions, cementation duration and temperature. The difference in the optimization of alloy additions was in the amount of addition of arsenic trioxide. The amount of 4%Sn-zinc alloy powder was tried to be optimized with the addition of arsenic trioxide whereas the optimization was tried to be done without any arsenic addition while using 10%Sn-zinc alloy. The XRD and SEM studies of the cementates were also performed.

The obtained results indicated that tin containing alloys were much better than pure zinc. With the additions of 4 g/l 4%Sn-Zn alloy dust, 1.2 g/l $CuSO_4.5H_2O$, 0.12 g/l As_2O_3 and in 2 hours of cementation duration at 85-90^oC, the maximum amount of cobalt cementation efficiency was achieved. The experiments indicated that cobalt in the solution could be reduced to about 2 mg/l by using 10%Sn-zinc alloy powder with an initial Sn/Co weight ratio of 13.25:1 without the addition of arsenic trioxide at 85^oC in 2 hours of cementation duration.

Keywords: Cobalt, precipitation, cementation, arsenic trioxide, zinc-tin alloy, purification

ÖZ

ÇİNKO ELEKTROKAZANIMI ÖNCESİ SEMENTASYON YÖNTEMİYLE KOBALTIN ÇİNKO SÜLFAT ÇÖZELTİSİNDEN UZAKLAŞTIRILMASI

Kayın, Pınar Burcu
Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Yavuz A. Topkaya

Ağustos 2003, 94 sayfa

Bu tezin amacı, kobaltın konvansiyonel metodla ve yeni katkı maddeleri olan %4 ve %10 kalay içeren çinko alaşımı tozları ile çöktürülerek çinko sülfat çözeltisinden uzaklaştırılmasıdır. Deneylerde sentetik olarak hazırlanan 150 g/l Zn ve 75 mg/l Co içeren liç çözeltisi kullanılmıştır. Konvansiyonel yöntemle yapılan deneylerde incelenen parametreler arseniküçoksit miktarı ve bakır sülfat eklenmesinin kobalt çöktürülmesi üzerine etkisidir. Çinko-kalay alaşım tozları kullanılarak yapılan deneylerde çalışılan parametreler arseniküçoksit miktarı, bakır sülfat ve çinko-kalay eklemeleri, çöktürme süresi ve sıcaklığıdır. Eklenecek olan çinko-kalay alaşımları miktarını belirlemek için farklı iki alaşımla yapılan deneylerdeki tek fark eklenen arseniküçoksittir. %4 kalay-çinko alaşımı miktarı çalışılırken çözeltiye arseniküçoksit ilavesi yapılmıştır. %10 kalay-çinko alaşımı miktarı çalışması ise arsenik katkısız gerçekleştirilmiştir. Çökeleklerin X-ışınları kırınımı (XRD) analizleri yapılmış ve çökelekler tarama elektronu mikroskobunda (SEM) incelenmiştir.

Elde edilen sonuçlar, çinko-kalay alaşımlarının saf çinkoya göre daha iyi olduğunu göstermiştir. Çöktürme verimi 4 g/l %4 Sn-Zn alaşımı tozu, 1,2 g/l $CuSO_4.5H_2O$, 0,12 g/l As_2O_3 ilavesi ile 85-90^oC sıcaklıkta ve 2 saat süre ile sınırlandığında en yüksek değerine ulaşmıştır. Arseniküçoksit kullanmadan çözeltideki kobalt miktarını 2 mg/l nin altına indirebilmek için başlangıç Sn/Co ağırlık oranı 13.25:1 olan %10 kalay-çinko alaşımı eklenmelidir; bu durumda deney sıcaklığı 85 ^oC, süresi ise 2 saattir.

Anahtar Kelimeler: Kobalt, çöktürme, sementasyon, arseniküçoksit, çinko-kalay alaşımı, saflaştırma

To my dear parents, Filiz and Yusuf Kayın…

ACKNOWLEDGEMENTS

I express my sincere appreciation to Prof. Dr. Yavuz Topkaya for his guidance and motivation throughout the thesis.

I would like to express my thanks to Benat Koçkar, Cengiz Tan and Ziya Esen for SEM analyses.

I also wish to acknowledge the help provided by Erdem Çamurlu, Semih Perdahçıoğlu and Tufan Güngören.

Thanks go to my roommate, Ender Keskinkılıç and Ebru Sarıgöl for their support in the completion of the thesis.

Sincere thanks are required for my family for their endless support and patience.

TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURE

CHAPTER 1

INTRODUCTION

1.1. General

Over 80% of the world's zinc is produced by the roast-leach-electrowinning (RLE) process. Advantages of the RLE process over pyrometallurgical alternatives include lower capital and energy costs, higher zinc recovery, and higher purity product. A disadvantage of the RLE process is that sulfur emissions are generated during roasting which produces a leachable calcine (1).

The commercial production of zinc by hydrometallurgy and the recovery of zinc metal by electrolysis was proposed and patented by Leon Letrange of France in 1881. First World War gave an added impetus to the developing of the electrolytic zinc process (2).

The zinc production methods employed today necessitate high treatment costs and consequently zinc metal producers demand high-grade concentrates. There are two main methods of zinc recovery from its ores, i.e., thermal reduction and electrolytic deposition. The purest zinc (%99.99) is achieved by the electrolytic methods. Most of the world's zinc is produced by the electrowinning of zinc from sulfate electrolytes.

In order to produce high quality zinc, more electropositive metallic impurities must be removed from the electrolyte prior to electrowinning. Cobalt is perhaps the most troublesome impurity due to its effect on current efficiency combined with the difficulty in removing it from the solution, so it must be removed from electrolyte because of the following reasons:

1. Cobalt, which is nobler than zinc, co-deposits with zinc, reducing the zinc quality and changing deposit structure and morphology.

2. Cobalt has lower hydrogen over potential than zinc; any co-deposited cobalt catalyzes hydrogen evolution at the expense of zinc deposition, reducing current efficiency considerably.

3. Hydrogen overpotential at the cathode creates a local increase in pH, which can lead to the formation of a passivating layer of zinc hydroxide or basic zinc sulfate on the cathode.

4. Cobalt interacts in a synergistic way with most other impurities, resulting in increased harmful effects (3).

Typically zinc electrolyte contains 10-20 ppm or mg/l cobalt, which the purification process ideally reduces to less than 0.1 ppm.

1.2. Aim of the Study

The removal of cobalt from zinc sulfate solution has been a focus of research for many years. The most common method is cementation. Cementation is the simplest and oldest hydrometallurgical process. It has been used in extractive metallurgy to recover valuable metals as well as to remove unwanted impurities.

The most common method used in industry is the cementation of cobalt with zinc powder. In order to achieve this goal activators such as As_2O_3, Sb_2O_3, etc., have been in use for a long time.

The aim of this study was to investigate alternative materials that could be used in the cementation of cobalt instead of zinc powder with or without As_2O_3 addition to the zinc sulfate solutions as an activator.

To decrease or eliminate the use of As_2O_3 as an activator, which is desired by the zinc industry because of health concerns, many alternatives, methods have been considered. Tin containing zinc alloy powders of two different compositions, prepared for this purpose, were tested for the removal of cobalt from artificial zinc sulfate solutions resembling in composition to that of Çinkur.

CHAPTER 2

LITERATURE SURVEY

2.1. Introduction

There are basically three main types of zinc ore on the Earth's crust. Those are oxidized, carbonated, and sulfur including zinc ores; however, most of the zinc ores are in sulfur including category (because they could not have enough time to be oxidized geologically). Metallic zinc has been marketed commercially for almost two hundred years with great changes taking place in its occurrence, methods of extraction and practical applications in pure, alloyed and compound forms.

It is normally accepted that zinc is not an easy metal to produce; it occurs mainly as a sulfide, often in conjunction with lead. Mining is reasonably conventional and the separation of the sulfide mineral by flotation is carried out readily. The sulfide mineral is normally converted to zinc oxide before reducing to the metallic form by aqueous or thermal routes. The arts of extracting zinc from its ores and of adapting zinc and its alloys and compounds to manifold engineering uses have developed of necessity with only fragmentary understanding of the physics and chemistry. However in recent years the sciences of physical chemistry and chemical thermodynamics have proved increasingly valuable, first in analyzing, controlling and improving existing technology and then as a basis for developing new methods of production (2).

Zinc is the 23rd most abundant element in the Earth's crust. Zinc is not found in the metallic state in nature. Sphalerite, zinc sulfide (ZnS), is and has been the principal ore mineral in the world. Smithsonite ($ZnCO_3$) is also the ore mineral of zinc. Some examples of these minerals are shown in Figure 2.1. In the United States, about two-thirds of zinc is produced from ores (primary zinc) and the remaining one-third from scrap and residues (secondary zinc). Zinc is necessary to modern living, and, in tonnage produced, stands fourth among all metals in the world production being exceeded only by iron, aluminum, and copper. Zinc uses range from metal products to rubber and medicines. About three-fourths of zinc used is consumed as metal, mainly as a coating to protect iron and steel from corrosion (galvanized metal), as alloying metal to make bronze and brass, as zinc-based die casting alloy, and as rolled zinc. The remaining one-fourth is consumed as zinc compounds mainly by the rubber, chemical, paint, and agricultural industries. Zinc is also a necessary element for proper growth and development of humans, animals, and plants; it is the second most common trace metal, after iron, naturally found in the human body (4-5).

COLLOFORM SPHALERITE (MORESNET/BELGIUM)	BANDED SPHALERITE (BAD GRUND/GERMANY)	SMITHSONITE (IRAN KUH/IRAN)

Figure 2.1. Zinc Ore Minerals

Zinc is mined in more than 50 countries and is produced as metal and compounds in about 40 countries. The largest deposits in the world are located in Canada, the world’s largest producer and exporter of zinc concentrates (6). In 1990, the leading ore-producing countries were Canada, Australia, and the U.S.S.R., in order of mine production; the leading metal-producing countries were the U.S.S.R., Japan, and Canada, in the order of primary smelter production. The United States accounted for only about 7% of world mine output and about 5% of world smelter production in the same year. This was not always so; during most of the 1900-1970 year period, the United States was the world's leading mine and smelter producer of zinc and, in the 1950's, accounted for more than one-half of world metal production. From the late 1960's to the mid-1980's, U.S. mine and smelter output declined by one-half and two-thirds, respectively. Mine production rose to former levels in 1989 and 1990 owing to the opening of a large zinc mine in Alaska. Smelter capacity, however, only marginally increased and, in 1990, was only about 40% of that of 1968 (4). The United States has been the leading world consumer of zinc since the early 1900's and currently consumes about one- seventh of world output. As a result of the substantial decline in domestic zinc smelter capacity, reliance on metal imports remains high. Ironically, the United States has become a major world exporter of zinc concentrate, but continues to be the world's largest importer of refined zinc.

In 2002, the total mine production of the world was 9,225,000 metric tons. In the same year, the total consumption (refined zinc consumption) of the world was 8,787,000 metric tons. Depending on data given in ILZSG (International Lead and Zinc Study Group), February 2002 (7), China was the leading world zinc producer and consumer. Some of the countries in zinc production and consumption in 2001 is given Table 2.1. The primary refined zinc capacity according to the continents is also illustrated in Figure 2.2.

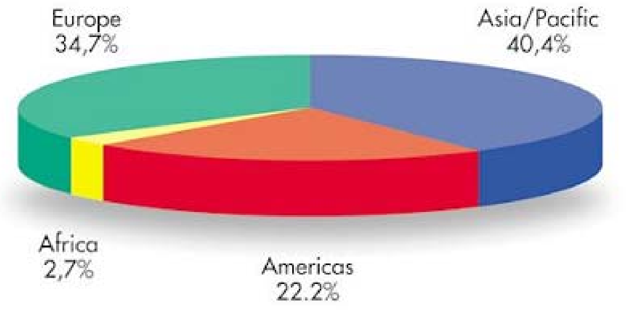

Figure 2.2. Primary Refined Zinc Capacity

Table 2.1. Zinc Production and Consumption by Country in 2001 (Figures given as thousand tons)

	Mine Production	Metal Production	Metal Consumption		Mine Production	Metal Production	Metal Consumption
Europe				**Asia / Pacific**			
Austria				Australia	1476	556	222
Belgium	-	256	265	Bangladesh	-	-	48
Bulgaria	11	88	10	China	1860	2078	1480
Finland	20	249	70	India	222	234	286
France	-	329	328	Indonesia	-	-	101
Germany	-	364	553	Iran	105	65	62
Greece	29	-	18	Israel	-	-	11
Ireland	298	-	3	Japan	45	644	633
Italy	-	183	355	Kazakhstan	350	266	35
Macedonia	20	52	10	Korea DPR	32	35	15
Netherlands	-	221	108	Korea, Rep.	5	508	411
Norway	-	145	34	Malaysia	-	-	50
Poland	145	175	110	Saudi Arabia	3	-	16
Romania	28	52	22	Taiwan, China	-	-	276
Russian Federation	164	250	150	Thailand	27	110	92
Slovak Republic	-	-	28	Turkey	46	2	84
Slovenia	-	-	15	Uzbekistan	-	35	8
Spain	185	427	218	Vietnam	28	-	40
Sweden	159	-	27	**Total Asia/Pacific**	**4200**	**4533**	**3997**
United Kingdom	-	87	190	**Americas**			
Yugoslavia FR.	4	10	10	Argentina	40	40	36
Total Europe	**1064**	**2888**	**2735**	Bolivia	147	-	-
Africa				Brazil	93	190	196
Algeria	7	26	11	Canada	1052	658	181
Morocco	107	-	9	Honduras	48	-	-
Namibia	41	-	-	Mexico	435	300	210
South Africa	62	109	89	Peru	1056	190	64
Tunisia	41	-	4	U.S.A	798	299	1141
Total Africa	**258**	**135**	**165**	**Total Americas**	**3702**	**1677**	**1891**

2.2. Cobalt

Cobalt derives its name from a German word, "Kobold", meaning mischievous goblins. Kobold ores were so named because these ores, when roasted, not only failed to yield copper, but emitted troublesome and dangerous fumes from the associated arsenic. About 95% of the cobalt produced in the world is obtained as a by-product of copper in Central Africa and nickel in other parts of the world. Only in Morocco is cobalt produced as a principal material from arsenide minerals. However, it should be mentioned that with the progress made in technology, it has become possible to increase cobalt production without having to produce more of the main metal.

The first use of cobalt can be traced to about 2600 B.C. in Egypt when cobalt compounds were used as colors for glass. Cobalt as a glaze dates back to about 1200 B.C. and cobalt compounds (mainly oxides) have been used as colors for enamels ever since.

Cobalt comprises about 0.02% of the Earth’s crust. Apart from a few primary arsenical ores in Morocco, Canada and U.S.A, cobalt is extracted as a by-product of nickel and copper but in small amounts extracted as a by-product of zinc (India) or precious metals.

Annual cobalt consumption is about 35,000 tons and until around 1985 approximately 80% of the world’s cobalt was supplied by La Generale des Carrieres et des Mines (Gecamines) and Zambia Consolidated Copper Mines (ZCMM) from the Copper Belt in Southern Africa. In the last decade the minor producers have increased their prominence in the market-place and a number of new sources have become available (8).

Cobalt is a group VIIIA metal, linked to iron and nickel. Like them, it is a silvery metal but is brittle at room temperature and its uses are invariably as alloys and rarely, in an engineering sense, cobalt is used on its own.

Some properties of cobalt are:

1. It has a high melting point (1495°C) and retains its strength up to a high proportion of it.

2. It is ferromagnetic and uniquely, is the only material which, if added to iron increases its saturation magnetization. Ferromagnetic materials lose their magnetic ability at a given temperature, the Curie point. Cobalt has the highest known Curie temperature at 1121°C.

3. Cobalt oxide when fused with silica and mixed with other oxides can form a range of colors/pigments from blue to yellow and even black.

4. Cobalt has the atomic number 27. Its electronic structure accounts for its variable valency. Cobalt^{+2} is the dominant ion but both Co^{+3} and Co^{+1} can occur. This property probably accounts for cobalt's wide use as a catalyst.

Unlike base metals such as copper and nickel, which are mainly used in electrical applications and in the manufacture of stainless steel, cobalt is used in many diverse applications. Approximately 55% of all cobalt used is in metallic form.

Cobalt is a strategic and critical metal used in many diverse industrial and military applications. The largest use of cobalt is in superalloys, as seen in Figure 2.3, which are used to make parts for gas turbine aircraft engines. Cobalt is also used to make magnets, corrosion and wear-resistant alloys, high speed steels, cemented carbides and diamond tools, catalysts for the petroleum and chemical industries, drying agents for paints, varnishes, and inks, ground coats for porcelain enamels, pigments, battery electrodes and magnetic recording media (9).

2.3. Cobalt Uses

2.3.1. Superalloys

The largest use of cobalt is in superalloys, which account for about 9,500 tons per year of refined cobalt (26% of total demand). The alloys are predominantly nickel based but they can also be cobalt or iron based. Cobalt is added to nickel alloys to improve high temperature properties. Cobalt also increases the solubility of carbon in the alloy matrix thereby modifying the grain boundary carbides formed. It also improves hot workability and reduces the stacking fault energy, the latter resulting in a reduction in the creep rate. The main uses are in the aerospace industry but in recent years they are being increasingly used in land based and marine turbines.

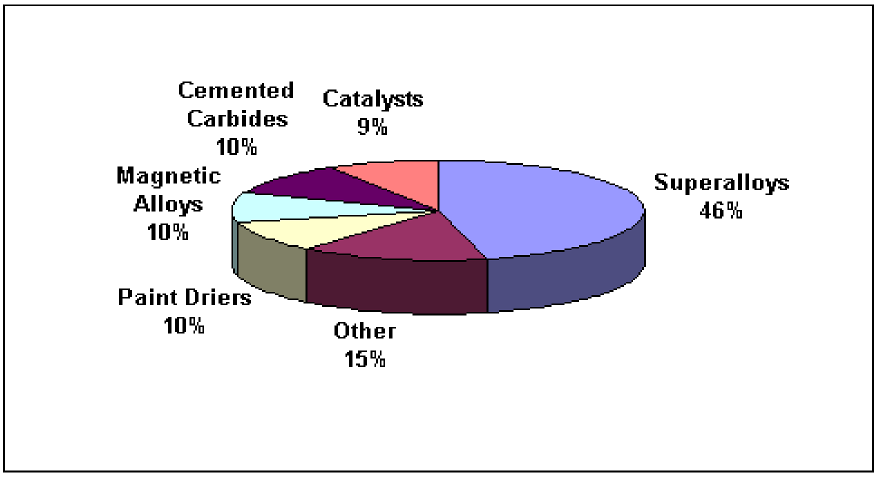

Figure 2.3. Domestic Uses of Cobalt in USA

2.3.2. Hard Metals

The "Stellite Alloys", originally developed in the early 1900's still have large markets. Stellite alloys are a family of cobalt-chromium alloys with various alloying additions. Their strength, erosion and corrosion resistance, castability and weldability have resulted in two important applications. Firstly, prosthetic parts such as knee and hip replacements and dental components are made from similar alloys. These are easily castable, allowing great detail and a highly polished surface. They also possess high hardness, wear resistance, corrosion resistance and biocompatibility.

Secondly, cobalt based alloys have been used in applications requiring high temperature wear and/or corrosion resistance for over ninety years. Many forms are available including cast and wrought components and hard-facing products such as wire, covered electrodes, powders etc (10-11).

2.3.3. Carbide Components

Probably the second most important use of metallic cobalt today is as a binder for carbide components. Of all the engineering materials, the sintered carbide-cutting tool has dominated the 20th Century. The base of the tool is tungsten carbide but it is the cobalt cement that allows the material to be used so effectively. Cobalt has the necessary properties of a good binder for carbides:

1. It has a high melting point.
2. It has high temperature strength.
3. It forms a liquid phase with WC at a suitable temperature 1275°C.
4. It dissolves WC to form a eutectic with a melting point of 1275°C.
5. It forms a hard but tough binder on cooling.
6. It can be ground to a very fine mix with the hard particles it has to bind.

Other materials have been and are being tried but none is as suitable as cobalt, which still dominates. About 4,500 tons of extra-fine (sub-micron) cobalt powder goes into the carbide industry each year.

2.3.4. Magnets

The hard magnets retain their magnetic properties and constitute a very important and sophisticated class of engineering materials. Permanent magnets have a wider range of industrial and commercial applications ranging from single bulletin board magnets to advanced magnets used in electronic devices. Advances in magnetic technology have enabled devices to become smaller and more energy efficient.

2.3.5. Other Metallic Applications

Cobalt is used in many other metallic applications, such as high-speed steels and controlled expansion alloys.

2.3.6. Cobalt in Chemicals

Chemicals account for about 45% of the world's total cobalt demand although the tonnage of individual compounds can be very small in certain industrial applications. Cobalt is a transition metal and the properties of these elements such as variable oxidation states; color and ability to form complexes lead to important commercial applications of cobalt chemicals. Some of them are given in Table 2.2 (11).

Table 2.2. Applications of Cobalt Chemicals

Adhesives	Electronic component
Anodising	Feed Supplement
Batteries	Moisture Indicators
Catalysts	Pharmaceuticals
Driers	Pigments
Electroplating	Solution Recording Media

2.3.7. Catalysts

The ability of cobalt to undergo oxidation-reduction reactions is thought to be important in its wide use as catalysts.

The largest of these applications is in the production of terephthalic acid (TPA) and dimethylterephthalate (DMT) for the production of polyethylene terephthalate (PET) for polyester fibers, recording tape, containers, food packaging, adhesives etc. The catalysts are generally mixed cobalt and manganese acetates in the presence of bromine containing co- catalyst.

The second major use as a catalyst is for hydroprocessing. Hydroprocessing is the general term for the catalytic process in which a hydrocarbon feedstock is reacted with hydrogen under pressure in the presence of a catalyst. In this process, undesirable impurities such as sulfur and nitrogen are removed from hydrocarbon feedstock. Global pressure on oil refineries to lower the level of sulfur in fuels is resulting in increased demand for hydrocarbon processing capacity.

Cobalt is also used as a catalyst in paint dryers and radial tyres in the form of cobalt carboxylates. These applications probably account for about 3,500 tons per year of cobalt. The compounds are commonly known as metal soaps. Many paints and inks are oil based which thicken and solidify by oxidation on exposure to air. The oxidation can take years in some cases and the function of the drier is as an oxidizing catalyst in the organic system to accelerate the process. Researchers for many years have concluded that "Cobalt is the fastest and best primary drier for paints and inks in common use today".

Another major use of cobalt soaps is in adhesives where it is used to promote rubber to brass coated steel adhesion in radial tyres. A typical radial tyre is a complex structure, which has to rely on bonding rubbers of varying hardnesses to a brass, coated steel and synthetic fiber casing. The bonding of the steel to the rubber has been one of the problem areas over the years and cobalt has become dominant in solving it. The bond is formed between the brass (Cu-Zn) and natural rubber. This bond relies essentially on the development of a film of copper sulfide. The durability of the bond can be adversely affected in a number of ways such as delamination of the CuS film or dezincification of the brass. Cobalt is believed to increase the cure rate of rubber and its cross-link density, form a strong CoS bond and lower the rate of brass sulfidisation and suppress dezincification.

2.3.8. Cobalt in Solution

Soluble cobalt compounds account for a considerable use of cobalt each year. Solutions of cobalt chemicals are used as feedstock for electroplating cobalt or cobalt alloys and electroless plating for providing a metallic coating on a non-conducting material, the most common being in recording media applications.

Cobalt is also essential to life. Perhaps the most important use of cobalt is in the treatment of pernicious anemia in humans and a group of animal diseases.

2.4. Source of Cobalt

Cobalt is not found as native metal except in meteorites, but occurs as sulfides, sulfo-arsenides and oxidized minerals (carbonates, arsenates, and complex hydrated oxides). More than 60 different cobalt minerals have been described, with cobalt contents running up to 60%. These cobalt minerals are associated in cobalt deposits with other valuable minerals and with the gangue, forming cobalt ores with cobalt contents varying from a trace to a few percent.

Cobalt is almost always produced as a by-product of other more abundant metals. Cobalt is usually mined as a co-product of either nickel or copper, or other more abundant metals. Most cobalt production is ultimately dependent on the production of copper and nickel. The mined ore often contains only 0.1% elemental cobalt. The ore is processed and the cobalt is extracted and converted to 99.9% cobalt metal.

The metal is sold to a cobalt chemical manufacturer who converts the metal to cobalt carbonate, cobalt sulfate, or other cobalt salt derivatives.

The United States is the world’s largest consumer of cobalt with no domestic mine or refinery production operations. Consequently, the U.S. is 100% dependent on imports for its supply of cobalt. A significant amount of the world’s supply of cobalt is produced in Africa. In 1985, Zaire produced about 45% of the total world mine production of cobalt. By 1996, the Congo (formerly Zaire) represented only 7% of the world’s production, as seen in Figure 2.4. Since 1991, U.S. imports from Africa have decreased; and, imports from Finland, Norway and Russia have increased.

Currently, more than one-half of the world's supply is produced as a by-product of copper mining and refining in Zaire and Zambia. Cobalt production in most other countries is a by-product of nickel mining and/or refining. Although some producers can increase or decrease the amount of cobalt mined or refined, most cobalt production is ultimately dependent on the production of copper and nickel.

The cobalt obtained from Zaire mainly occurs as the copper-cobalt oxide heterogenite. This mineral is obtained from open-pit mines, and the crude ore is crushed and milled before concentration of the metal-bearing fraction by froth-flotation. In this latter process the milled ore is suspended in an aqueous medium through which air is blown and to which specific frothing and surface-active agents are added. These selectively carry the valuable mineral from the unwanted gangue.

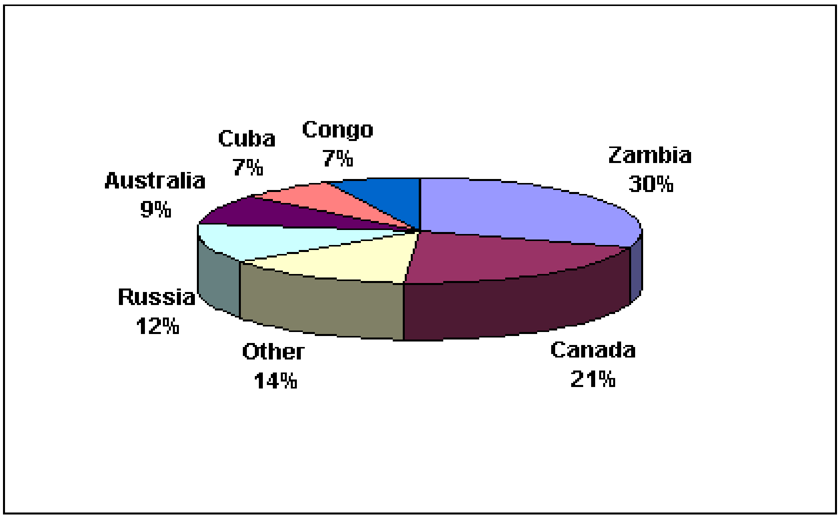

Figure 2.4. The Cobalt Production of the World (1996)

The cobalt-rich oxides, with roughly equal copper and cobalt contents, are then sintered to pellets and fed to electric smelting furnaces along with selected high-grade ores, which are suitable for smelting without prior concentration. The furnace charge includes lime and coke to provide reducing conditions. The molten product is separated by density difference into two metallic fractions, a heavy “red alloy”, containing 90 percent copper, 5 percent cobalt, and 4 percent iron, a lighter “white alloy” containing about 42 percent cobalt, 15 percent copper, 34 percent iron, and 2 percent silicon. The copper-rich red alloy is smelted in the copper plant, and the cobalt content is then transferred to a slag, which is returned to the furnace charge for the original cobalt smelting furnaces.

Cobalt is also recovered from the copper oxide ores containing much smaller proportions of cobalt, in the order of 1 part cobalt to 25-30 parts copper. These minerals, after concentration by crushing, milling, and flotation, are dissolved in sulfuric acid and the copper electrolytically extracted. The cobalt remains in the solution, and the spent electrolyte is given further chemical and electrochemical treatments to remove all remaining copper, before being treated with lime to precipitate the cobalt as hydroxide, together with small contents of nickel, zinc, manganese, and magnesium. The hydroxide is fed in suspension to a neutral electrolyte from which it is electrodeposited on to mild steel cathodes. The deposit contains 92-94 percent cobalt, the principal impurities being zinc, nickel, and manganese. It is then refined by arc-furnace melting, deoxidized, and desulfurized, and the cobalt is granulated and screened to give a product of about 99 percent purity.

2.5. Minerals of Cobalt

The most important cobalt containing minerals are listed as follows:

Erythrite ($3CoO.As_2O_5.8H_2O$): Its characteristic bright red-purple color is very noticeable and was used to spot veins of cobalt-bearing ore. Earthrise (hydrated cobalt arsenate), or "Cobalt Bloom" as it is called by miners, is a weathering product of cobalt-containing minerals such as cobaltite. Most erythrite is found in the form of crusts, but specimens from Morocco have larger crystals.

Skutterudite ($(Ni,Co)_xAs_y(CoAs_3)$): Skutterudite is the cobalt-rich end member of a series (Smaltite ($CoAs_2$), Chloanthite, or Ferro-Arsenite) in which nickel or iron replaces part of the cobalt. Enough nickel is usually present to make skutterudite a significant mineral of nickel. The iron rich variety is rare.

Safflorite $(Co, Fe)As_2$: Safflorite is a rare mineral, but is found with other arsenides and thus it is included with them when mined for cobalt and/or arsenic (12).

Carrolite ($CuCo_2S_4$), Linnaeite $(Ni, Cu, Fe, Co)_xS_y(Co_3S_4)$, Cobalt oxides ($CoO$, Co_2O_3), Roselite ($Ca_2(Co, Mg)(AsO_4)_2.2H_2O$) are the other cobalt containing minerals.

2.6. Zinc Electrowinning

In the roast-leach-electrowinning process, shown in Figure 2.5, zinc concentrates containing 50-65% zinc as sulphides are roasted to form a calcine consisting primarily of zinc oxide. The calcine is leached in an acidic solution containing sulphuric acid and zinc sulfate. Precipitated iron hydroxides are removed from the resulting neutralized solution and additional impurities are removed by cementation with atomized zinc. Zinc is recovered from the purified solution by electrolysis. In electrolytic production of zinc, cobalt is removed from the zinc electrolyte by cementation with zinc dust prior to electrowinning.

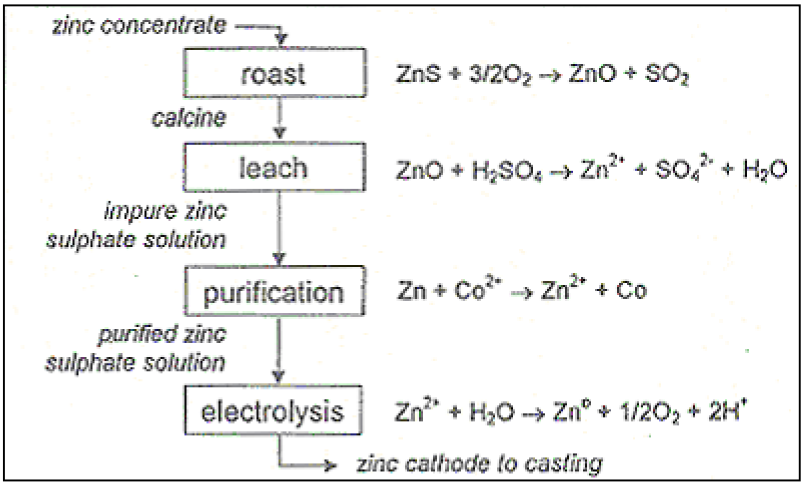

Figure 2.5. Roast-Leach-Electrowinning Process

Although the thermodynamics for this reaction are favorable kinetic barriers to cobalt reduction render the method almost useless in practice unless activators such as copper and antimony or arsenic are added.

Zinc concentrate mainly consists of insoluble zinc sulfide; roasting converts this into soluble zinc oxide. Leaching the roasted concentrates with sulfuric acid liberates zinc ions as well as impurities such as iron, copper, cadmium, cobalt and nickel; the solution must then be purified before becoming the feed to the electrolysis step from which metallic zinc is recovered.

The zinc electrowinning process is unusual from a thermodynamic point of view because zinc has a more negative reduction potential than hydrogen; one would expect hydrogen gas to evolve at the expense of zinc deposition. However, zinc metal is electrowon economically from acidic zinc sulfate solution because hydrogen has a high overpotential on zinc metal. In order to maintain this large overpotential, impurities in the leach solution must be completely removed.

$2H^{+}+2e^{-}\Rightarrow H_2$ $E^{o}=0V$ Eq.2.1.

$Zn^{+2}+2e^{-}\Rightarrow Zn^{o}$ $E^{o}= -0.76\ V$ Eq.2.2.

The driving force for this reaction is the electrochemical potential assumed by metals in contact with ions in the solution. The more electropositive ions are precipitated as metals from solution by cathodic reactions. A competing reaction to metal precipitation is the reduction of H^{+} ions to hydrogen gas. To minimize this competing reaction, the cementation process is operated at a low acid concentration (pH 5).

Remaining traces of impurities co-deposit with zinc or act as catalysts for the competing reaction to zinc deposition (hydrogen evolution), causing large drops in current efficiency.

Cementation process is the method to get rid of impurities. It is a heterogeneous reaction between two metals in which the less noble metal displaces the ion of a more noble metal from solution when placed in contact with it. Therefore, cobalt ions deposit on the surface of the less noble zinc dust, which, in turn, progressively dissolves (13).

$Co^{+2}+Zn^{\circ}=>Co^{o}+Zn^{+2}$ $E^{o}= +480$ mV at 25 °C Eq.2.3.

Thermodynamics predict the cobalt removal should not be a problem, since zinc is more electronegative than cobalt; therefore, the latter should precipitate out as cobalt metal upon zinc dissolution. Lawson and Nhan calculated the ΔG^{o} of the reaction at 25°C to be –93 kJ/mole of cobalt with an equilibrium constant of $2* 10^{16}$. An equilibrium constant of this high magnitude suggests that cobalt ions should be completely removed from aqueous solution with metallic zinc, no back reaction would be expected (14).

In practice, however, cobalt cementation is very slow due to kinetic barriers. Thermodynamics provide information about at which direction a reaction will proceed but it can not predict its reaction rate. The extremely slow kinetics of the cementation reaction of cobalt on zinc means that "activators" are required, that is elements which enhance the rate of cobalt cementation and render the cementation process viable. It has been found that cobalt cementation can be improved considerably by using activators, additions to the electrolyte which increase cobalt cementation. Industry currently uses mainly two cementation methods: activation with arsenic and copper or with antimony and copper.

It is commonly believed that these activators form the cathodic site on which hydrogen evolution and cobalt deposition takes place. It is believed that activators perform by:

1. Increasing the cathodic surface area
2. Increasing the hydrogen over-potential on zinc and on cobalt rich areas, and
3. Forming intermetallic compounds or alloys that have a high overpotential (15).

In the cementation reaction, anodes and cathodes behave as short-circuited cells, and share the mixed potential.

Furthermore, the metal surface is simultaneously subjected to deposition and dissolution, which leads to changes in cathodic/anodic area ratio depending on the nature of the deposit. This can result in changes to mixed potential system, and the driving force of the cementation reaction.

Kinetics of cobalt cementation processes can be expressed by:

$$-dC_{Co}/dt = k.A/V.C_{Co} \qquad \text{Eq.2.4.}$$

where; dC_{Co}/dt=Cobalt precipitation rate, k=rate constant, C_{Co}=Cobalt concentration, A=catalytic zinc surface area, and V=solution volume.

Equation indicates that the mass transfer mechanism is largely governed by the A/V ratio, i.e., it is directly proportional to the reactants available catalytic surface area for the reaction and inversely proportional to the volume of the solution, in a batch operation. Thus, decreased particle size and increased precipitant concentration is desirable. For nearly 75 years, however attempts at increasing the total mass of reactant per unit volume have met with little success. For batch cobalt purification, the A/V ratio is frequently arranged to yield retention times between 2-4 hours. These times are, however achieved at the expense of a large excess of zinc dust. In continuous operation, the solution passes through a cascade of agitation tanks as fresh zinc dust is added to each tank. This improves zinc consumption since, at lower cobalt concentrations, a larger catalytically active zinc surface is still available.

High zinc dust consumption and poor cobalt cement quality are significant drawbacks that inhibit conventional cobalt purification in stirred tanks. Zinc dust consumption quite more than the stoichiometric requirements is caused by discharging excess, cobalt, nickel, cadmium-covered, zinc particles and by zinc oxide layer dissolution via acid addition. The oxide covering layers are formed while producing zinc dust and during the purification reactions.

For a continuously operated reactor, Eq.2.4 becomes;

$$\frac{C_{Co}}{C^{0}_{Co}} = \exp\left(-k.\frac{A}{V_f}\right) \qquad \text{Eq.2.5.}$$

where; C^{o}_{Co}= initial cobalt concentration, C_{Co}= final cobalt concentration, A= catalytic zinc surface area, V_f= solution flow rate= V/t, t=retention time.

2.7. Methods of Solution Purification of Zinc Electrolyte

The presence of impurities in a zinc electrolyte solution is problematic for the electrowinning process. Impurities act as catalysts for hydrogen evolution, which leads to a large drop in current efficiency (CE). Therefore, adequate purification of the zinc electrolyte before electrowinning is essential (16).

It is generally believed that the alkali and alkaline earth metals are not detrimental in the electrowinning of zinc. In fact, Ault et. al., showed that the current efficiency increases slightly with the addition of high concentrations of sodium and potassium to the electrowinning solution (17). The authors suggested that such ions act by an adsorptive mechanism, which inhibit the action of hydrogen on zinc deposition. However, there is also evidence that zinc ions inhibit the hydrogen evolution reaction rather than the reverse.

One can generally say that; ions of those metals with standard potentials more negative than zinc, such as Al, Mg, Ca and Na have little effect on current efficiency; ions of metals with standard potentials marginally more positive than zinc, such as Cd and Pb, tend to deposit at the cathode, decreasing its purity; ions of those metals with standard potentials much more positive than zinc and which are characterized by a high melting point and low hydrogen overpotential such as Pt, Ag, Au, Fe, Co, Ni, Cu decrease current efficiency. Metals like Sb, As, Ge, Se, Te act in a more complex manner; they can form hydrides which serve as the cathodic reaction for localized corrosion, making it possible for zinc to redissolve even while cathodically polarized (3). The effect of those metals is shown in Figure 2.6.

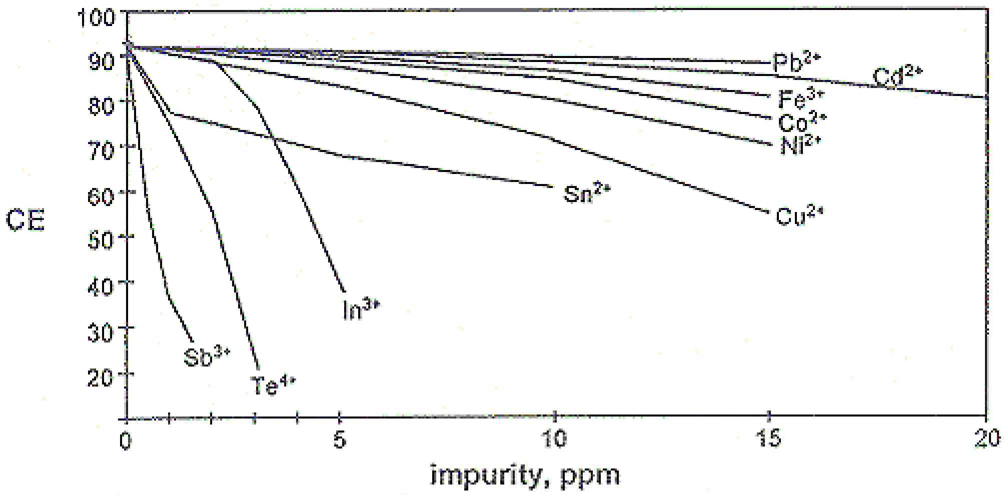

Figure 2.6. Effect of Impurities on Zinc Electrowinning Current Efficiency

The removal of cobalt from the solution is critical. Many papers and patents describe the increase in the cobalt cementation rate due to addition of metal ions. Taking into consideration zinc dust cementation and the complexing characteristic of cobalt with certain organic compounds, different processes have been developed and are being practiced all over the world depending upon the impurities present in the impure zinc sulfate solution especially cobalt after neutral leach. The purification processes that are being adopted to remove the cobalt content from the zinc sulfate solution are:

1. Cold Beta Purification
2. Cold-Hot Purification or Modified Cold-Hot Purification
3. Arsenic Trioxide Purification
4. Solvent Extraction Method
5. Cementation of Cobalt by Suspended Zinc Particles in the Presence of Copper or Antimony with Certain Surfactants

6. Extraction of Cobalt with P507
7. Cobalt Precipitation by Reduction with Sodium Borohydride
8. Cobalt Cementation with Ferromanganese
9. Oxidation-Precipitation of Cobalt using Caro's Acid
10. Manganese Dust Purification
11. New Type of Zinc Powder Purification
12. Molecular Recognition Technology for Cobalt Removal
13. Xanthate Purification

2.7.1. Cold Beta Purification:

In this process zinc dust is added to cement out copper, cadmium, and nickel in the first stage. Following the preparation of reagent that is known as alpha-nitroso-beta-naphthol, which consists of beta naphthol, sodium nitride and caustic soda that are previously dissolved and mixed, second stage starts. A1pha-nitroso-beta-naphtol is added into the solution (pH value is adjusted around 2.8) for the removal of cobalt followed by activated charcoal treatment to remove the excess organic as seen in Figure 2.7.

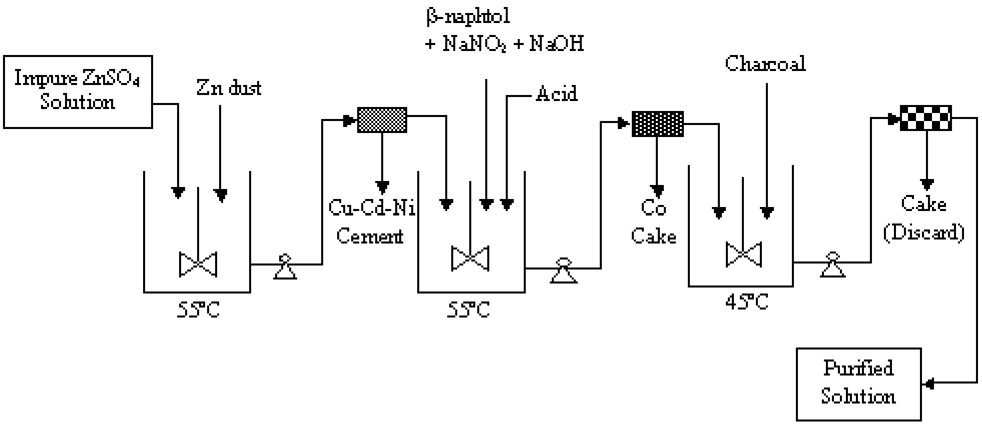

Figure 2.7. Cold Beta Purification

The use of α-nitroso-β-naphthol as additive has an adverse effect on the subsequent electrolysis, and requires an additional treatment for its abatement.

There are many reagents that complex with cobalt but only a few gave the desired extraction. The most promising were α-nitroso-β-naphthol, β-nitroso-α-naphthol, 1,2-cyclohexane dione dioxime (nioxime), di-2-pyridyl ketone oxime and dimethylglyoxime. All of the complexing reagents have the organic functional group of oximes (-NaOH). Oximes are known to complex with many of the metal ions. They are the base for several commercially available solvent extraction reagents and ion exchange resins.

The use of α-nitroso-β-naphthol resulted in the extraction of >99 pct of the cobalt at a pH of 3.5 in the diluent kerosene-isodecanol. Ninety percent of the cobalt was extracted in benzene.

The primary difficulty in using either of these is that the cobalt can not be stripped from the organic phase because it is oxidized to cobalt (III). 75 to 80% of the cobalt was extracted at a pH of 5.2 in the diluents toluene-isodecanol and kerosene-isodecanol (18). One of the advantages of cold beta purification process is the low operating temperature because the solution does not require excessive heating. Another advantage is the small amount of zinc dust loss during the operation (19).

2.7.2. Cold-Hot Purification

In cold-hot purification, cadmium, copper and nickel are cemented out by the addition of zinc dust under cold conditions (50^{o}C) and cobalt in the second stage at hot conditions (90^{o}C) by the addition of zinc dust in the presence of antimony compounds, mainly antimony trioxide or potassium antimony tartarate (PAT) (Figure 2.8). When Sb^{+3} is used as a cobalt cementation aid, it is usually added as potassium-antimony-tartrate. Tartaric acid, HOOC-CHOH-CHOH-COOH, is dicarboxylic. Tartrate forms complexes easily, and masks a wide range of metal ions. The reactions for the antimony trioxide purification process can be expressed as follows:

$Co^{+2}+2HSbO_2+Cu^{+2}+6H^++10e^- = Cu\text{-}Co\text{-}Sb(alloy)+4H_2O$ Eq.2.6.

$Zn^o=Zn^{+2}+2e^-$ Eq.2.7.

or

$Co^{+2}+HSbO_2+5/2Zn+3H^++10e^-=CoSb+2H_2O+5/2Zn^{+2}$ Eq.2.8.

Van der Pas and Dreisinger showed that the cement from a solution containing zinc ions is mainly zinc with very little cobalt (>98%Zn) (20). In fact, zinc free cobalt deposits can not be obtained from sulfate solutions even when Zn^{+2} is present only in traces in the solution.

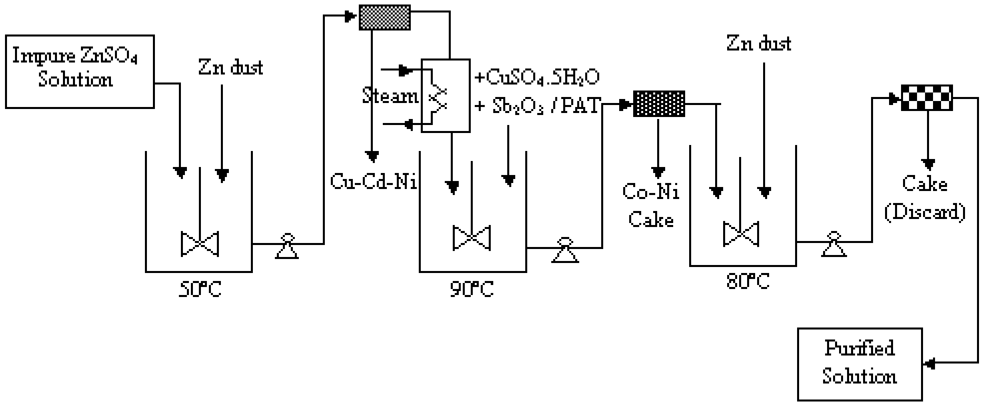

Figure 2.8. Cold-Hot Purification

Several mechanisms have been proposed for the role of copper and antimony in enhancing cobalt removal. Most of those mechanisms fall in the category of alloys (intermetallics) and substrates. The activators either form a preferential substrate for cobalt deposition or co-deposit with cobalt as a nobler alloy (21). Antimony greatly improves the rate and extent of reaction, while copper and antimony together give the best removal rate. Sb(III) undergoes preferential reduction by zinc:

$Sb^{+3}+3e^-\rightarrow Sb^o \quad E^o= 0.152\ V$ Eq.2.9.

Data in scientific sources point that antimony has a weaker effect on activated cementation compared to arsenic. In most plants, however, antimony compounds are used as activators because of the higher toxicity of arsenic compounds.

An early study by DeBlander and Winand (21) showed that the formation of antimony, copper, and cobalt triple alloys accelerate cobalt deposition and inhibit hydrogen evolution. According to their study copper has a greater accelerating effect, while antimony stabilizes the deposit. It was found by Lew (1) that the cobalt cementation was improved considerably with small additions of copper and antimony. Lew observed that antimony alone activates cobalt reduction, but the final cobalt concentration is much higher than when antimony and copper are both present, and the rate of cementation is slower. The cement layer on the zinc dust contained a mixture of copper, cobalt and antimony but primarily zinc (70-98%). Fontana and Winand examined cementation residues for alloys formed (22). They identified CoSb and $CoSb_2$ in the cement by X-ray diffraction (XRD); the characteristic peaks for antimony or cobalt alone were not observed. They concluded that antimony acts to diminish the cobalt reduction overpotential on zinc by forming definite alloys. Kroleva (23) claimed that copper and antimony co-deposit onto the zinc dust as Cu_2Sb, which acts as a preferential cathodic substrate for cobalt deposition. This alloy would exhibit a decreased overpotential for cobalt reduction and an increased overpotential of hydrogen evolution. However, the formation of copper-antimony was not verified.

According to the observations of Fountoulakis, cobalt forms a ternary alloy or a solid solution with Cu and Sb (15). MacKinnon systematically studied the effects of impurities. By addition of antimony, he has identified the intermetallic compounds CoSb and $CoSb_2$ from the X-ray diffraction analysis of the precipitate at the end of the reaction (24). DeBlander et al. (21) and Fountoulakis (15) attributed the beneficial effect of copper and antimony to the formation of cobalt alloys with increased nobility and a reduced cobalt activity. Because of its high nobility, copper was said to have the highest accelerating effect on cobalt removal kinetics; whereas, antimony was claimed to act as an alloy stabilizer between cobalt and copper.

Recently, van der Pas (20) confirmed the difficulty in cementing cobalt by zinc dust from a zinc electrolyte and attributed it to the inhibition of cobalt reduction by zinc ions. In the presence of zinc ions, cobalt can not be deposited in a pure form, but it was deposited as a cobalt-zinc alloy, which was consisted primarily of underpotentially deposited zinc. They also reported that the addition of soluble copper and antimony to the electrolyte improved the rate and extent of cobalt cementation. Continuous N_2 sparging of the solution was also recommended to prevent it from the redissolution of the precipitated cobalt by oxidation due to dissolved oxygen. The scanning electron microscopy (SEM) results indicated that copper and antimony cemented out of solution in the early stages of cementation process, forming a preferential substrate for cobalt deposition. Nelson et al. (25) also reported that the presence of zinc ions inhibited cobalt reduction. But this did not occur when activators such as antimony were present. They suggested that activators formed a preferable substrate for cementation as most of the scientists mentioned above. They tested eight new activators; namely, Sb (III), Sn (II), Pb (II), Bi (III), Se (IV), Te (IV), In (III), Hg (II). At least two of the newly tested activators, that were tin and tellurium, showed a promise of equal or better performance than antimony in terms of both cobalt cementation and reduced zinc dust consumption. They also indicated that the hydrolysis of the metal could be an important step in the activation mechanism. More clearly, the hydrolysis product was adsorbed on the zinc dust surface, where the metal could then be reduced.

Many tests were performed looking at different parameters. Process parameters and electrolyte composition have a considerable effect on the kinetics of copper-antimony activated cobalt cementation. A large zinc dust surface area in the form of a high dust loading or small sized dust gives a large reaction area and, therefore, increases the cobalt cementation rate. The optimum solution pH is a compromise between minimizing hydrogen evolution at a low pH and the precipitation of basic zinc compounds at a too high pH. Increasing the temperature has a beneficial effect on cobalt cementation kinetics because cobalt cementation is a chemically or electrochemically controlled process with activation energy of 86.6 kJ/mol (1).

The solution pH affects the rate of cementation, although Blaser and O'Keefe suggested that this is the least influential parameter among temperature and reagent concentrations (26). The pH changes between 4.0 and 4.4: although it is important to maintain as high a pH as possible in order to decrease the hydrogen ion activity and minimize hydrogen evolution, if the pH is too high there is a risk of forming basic zinc sulfate or zinc hydroxide which slows the process by forming a passivating layer on the zinc dust surface. Van der Pas and Dreisinger (20), however, argued that increasing the pH beyond the point where basic zinc compounds form does not inhibit the reduction of cobalt. Borve and Ostvold found that the initial cementation rate is slightly higher for solutions at pH 4, but that the final cobalt concentration is independent of initial pH (27). So the experiments were done at pH=4.

The presence of Cd and Cl also affect the cementation rate. Cadmium in small quantities is beneficial. Addition of up to 100 ppm Cd^{+2} acted synergistically with Sb/Cu, bringing the final cobalt concentration even lower than the levels obtained with Sb/Cu alone(25). Although a small amount of Cd^{+2} has a positive effect, increasing the Cd^{+2} concentration results in progressively higher final concentrations. This is an important consideration in purification circuits that remove cadmium completely prior to cobalt cementation.

The presence of large amount of chloride improves cobalt cementation. Sometimes controversial results are obtained as to the influence of activators. Thus, the simultaneous usage of Cd and Pb is not recommended and, on the other hand, one of the recommended combinations of activators is Sb-Pb-Cu-Cd.

Problems with the redissolution of cobalt from the precipitate were also experienced in cold-hot purification. Whenever a batch of solution was held up, due to some problem, and slurry could not be filtered, cobalt levels was used to rise in the solution (19).

The antimony process typically operates at a higher temperature (98°C) than arsenic (70-75°C) but uses smaller concentration of additive. Little is known about the mechanism by which these additives work, particularly the way copper and antimony or arsenic work in conjunction, thus this has been the focus of the majority of cementation research (3).

Antimony is injurious when 1 ppm or more present in purified solution. Its effects can be minimized by better solution purification, shortening the deposition period, and lowering the cell temperature.

A recent study at McGill University, in collaboration with Noranda/CEZinc, looked into the role of chloride, cadmium, and lead ions on the efficiency of the cobalt cementation process in conjunction with the antimony.copper activation process (16). In addition, many other elements were investigated as substitutes for antimony. As a result of this study, it was determined that cadmium and lead act synergistically with antimony and copper, which result in consistently lower terminal cobalt levels, and significantly lower zinc-dust dissolution. In addition, the same work found tin to be an effective substitute for antimony with respect to the overall kinetics. Before this study, another work was conducted at 95°C using a synthetic electrolyte solution containing 30 ppm cobalt by the same group in order to obtain the target cobalt concentration of 0.1 mg/l with minimum zinc dust consumption. The additives were present at 30 mg/l and a fixed amount of zinc dust of 5 g/l was used.

Various combinations of co-additives with antimony or tin were investigated at temperatures between 85°C and 95°C, initial cobalt concentrations between 8 and 30 mg/l and initial zinc dust concentrations of 2-5 g/l. The pH was kept constant at 4.

Electrolytic plants operating at relatively high current densities, 700 amp/m^2 for example, require electrolytes of exceptional purity. Such operating conditions require the use of arsenic for solution purification, because antimony would not satisfy the extremely high requirements for purification. Electrolysis at lower current densities, which is the practice in most modern tank houses, is less susceptible to impurities. For this application, the addition of antimony as an activator is satisfactory (28).

There are some technical and economic advantages of cold-hot purification:

1. It is a continuous, single stage process
2. A single purification residue is produced
3. Use of antimony is less polluting
4. Zinc consumption is lowered by as much as 40%.

On the other hand, the modified cold-hot purification is a newly developed technology; but is being practiced only by Hindustan Zinc Plants at 80-90^{o}C with additional/optional two-stage polishing operations. This involves a single-stage purification with two-stage operation using potassium antimony tartarate, copper sulfate and zinc dust for the removal of impurities as seen in Figure 2.9. The optimized conditions are given as: pH around 4.5-4.6, temperature approximately 80-85^{o}C, antimony added as PAT about 1 mg/l and a reaction time of 3-3.5 h with minimum (25 mg/l) amount of copper (29).

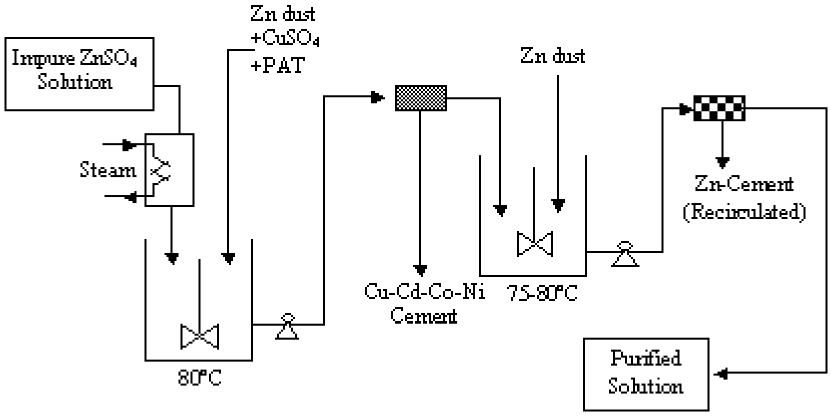

Figure 2.9. Modified Cold-Hot Purification

2.7.3. Arsenic Trioxide Purification

Arsenic trioxide purification is applied at two consecutive cleaning stages. At the first stage at temperature 80-90°C, As_2O_3 as solid powder or saturated in water is fed with zinc dust and copper sulfate into solution. At this stage cobalt left in solution is decreased to less than 10 mg/l at about pH 4. This is essential in order to get a high current efficiency at the electrolysis stage after the overall purification.

The presence of cobalt also compounds the damage caused by germanium. If germanium is present in zinc sulfate solution, the cobalt level should be decreased ideally to less than 0.2 mg/l. On the other hand, 3-4 mg/1 of cobalt in electrolyte is considered desirable because it tends to reduce the amount of lead in cathode metal. A cementate with high copper grade is obtained at the end of the first stage of purification. This cementate is filtered in pressure filters.

In the second stage in order to remove cadmium in the solution the temperature is decreased generally by water cooling down to 60-80°C and zinc dust is added if necessary as an activator. A cementate with high cadmium grade as well as copper is obtained. Then, after pressure filtering again, the cementates from first stage and second stage are processed together or separately to obtain cadmium and copper as by-products. The purification system is shown in Figure 2.10.

At the beginning at the electrolytic zinc plant in Kokkola (Finland), normal hot arsenic-zinc dust purification was used for the removal of cobalt, and zinc powder purification for the removal of cadmium. The process was a batch process. Immediately after the start-up, investigations of the purification of the zinc sulfate solution were started. As a result of these investigations, also the purification process was changed in connection with the expansion. In practical operations such as those of Kokkola (Finland) and Iijima (Japan), the purification process is composed of three steps- the elimination of copper with zinc dust, the removal of cobalt with zinc dust and As_2O_3, and cadmium precipitation by zinc dust in fluidized vessels (30).

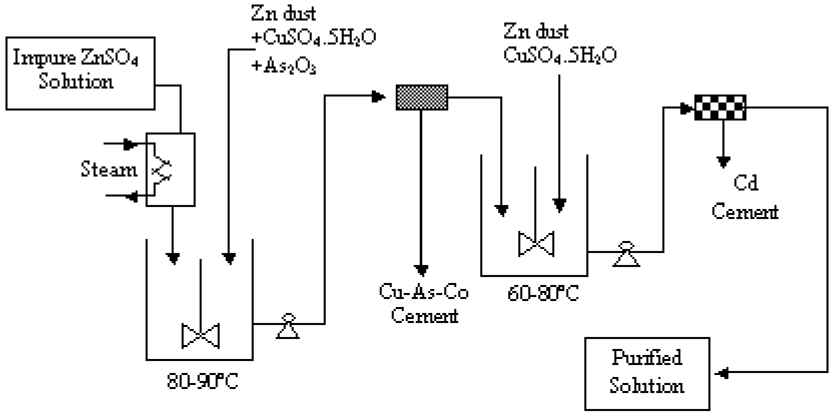

Figure 2.10. Arsenic Trioxide Purification

The solution purification comprises three stages. In the first stage, the copper is removed with zinc dust in a continuous process. The copper residue is separated in thickeners and the solution continues to the cobalt and nickel removal. These metals are removed with zinc dust and arsenic trioxide in an automatic batch process. The solution is filtered on filter presses, and the clear solution goes to the third stage in which the cadmium is removed in fluidized bed reactors using a zinc dust bed. The solid material is removed from the purified solution in hydrocyclones. After this, the solution is ready to be fed to the cell house.

Many studies suggest that additives act by forming alloys with cobalt; these alloys may be more stable than cobalt alone. Tozawa developed M-As-H_2O potential-pH diagram, which shows that metal arsenides for Cu, Co and Ni are all more stable than the metals alone, as it is seen from Figure 2.11.

The "hot arsenic-zinc dust" precipitation is carried out according to standard performance. A drawback of this cobalt removal process is the quite high surplus of zinc dust that has to be used. Most of this surplus is leached according to the reaction:

$$Zn+2H_2O=Zn^{+2}+2OH^{-}+H_2 \qquad \text{Eq.2.10.}$$

And thus the solution becomes more basic. If the amount of the zinc dust reacting according to the above reaction is high enough, the alkanity of the solution increases until it reaches the point where $Zn(OH)_2$, or more correctly, basic zinc sulfates $[3Zn(OH)_2.ZnSO_4.5H_2O]$ start to precipitate. At this point the zinc dust is passivated and the cementation reactions will cease. When the cobalt and nickel contents of the raw solution were high, a higher zinc dust surplus had to be added, and it happened quite frequently that the passivation point was reached before the cobalt was sufficiently removed.

The main hypothesis is that the cemented cobalt forms an alloy with zinc or with the ions added to the electrolyte. Many detailed explanations have been given:

1. Copper forms a larger cathodic surface for cobalt deposition and creates small galvanic cells that are suitable for cobalt deposition.
2. Cobalt cements on newly formed nuclei of metals nobler than cobalt
3. Cobalt cements as CoAs.
4. Cobalt cements as $CoAs_2$.

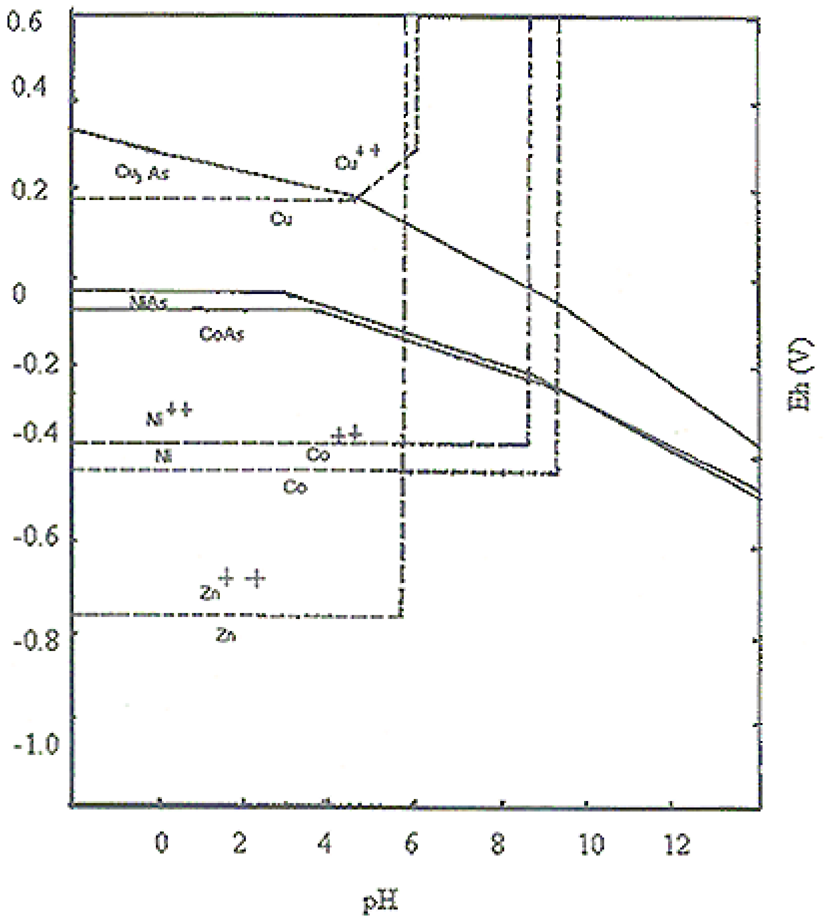

Figure 2.11. Potential-pH Diagram for the M-As-H_2O System (31)
([Cu] = [Ni] = [Co] = [As] = 10^{-5} mol/l, [Zn] = 1 mol/l)

Therefore, the reaction for the arsenic trioxide purification process can be expressed by the equation 2.11:

Co^{+2}+ $HAsO_2$ + $3H^+$+ 5/2 Zn=CoAs +$2H_2O$+5/2Zn^{+2} Eq.2.11.

The studies conducted by Tozawa et. al. (31) mentioned above supports the arguments given by Fugleberg et. al. (32). According to Tozawa et. al. and Fugleberg et. al. studies, “when examining the precipitates by microprobe in order to locate Co and Ni in the Cu_3As, it was surprisingly found that Co and Ni were not mixed with Cu compounds to a great extent but that Co and Ni were in separate compounds with As and that this was substantially Cu-free". They had detected that the Co, Ni, As particles were large and well defined also in a precipitate containing as much as 60% of Cu and only about 2% of Co and 1% of Ni. This led to the conclusion that Co (and Ni) are separated out as a pure arsenic compound, which later on was proved to be CoAs (or quite close to this stoichiometric compound). This meant that Cu could not be inevitable in the cobalt cementation.

The later studies showed that Co could be successfully precipitated with no Cu at all in the solution; however, small amounts of Cu in the solution are beneficial. Moreover, it was observed that the same concentration of Cu as of Co would give very satisfactory results.

It was found that the cobalt cementation rate was increased when arsenious oxide was present in conjunction with copper. Copper alone or arsenious oxide alone resulted in decreased cementation rates. These findings were consistent with those of Fugleberg (33), i.e., the arsenic system depended on the formation of a CoAs species that could be easily deposited on the copper substrate with a low overpotential. The most important suggested reactions taking place in cobalt and nickel removal step can be also given as follows (32):

$$Co^{+2} + As^{+3} + 2.5Zn^{o} = CoAs + 2.5Zn^{+2} \qquad \text{Eq.2.12.}$$

$$Ni^{+2} + As^{+3} + 2.5Zn^{o} = NiAs + 2.5Zn^{+2} \qquad \text{Eq.2.13.}$$

$$3Cu^{+2} + As^{+3} + 4.5Zn^{o} = Cu_3As + 4.5Zn^{+2}. \qquad \text{Eq.2.14.}$$

$$Cu^{+2} + Zn^{o} = Cu^{o} + Zn^{+2} \qquad \text{Eq.2.15.}$$

$$2H_2O + Zn^{o} = H_2 + Zn(OH)_2 \qquad \text{Eq.2.16.}$$

It was mentioned in the study of Fugleberg et.al. (33), that all the reactions listed above were chemically and not diffusion rate controlled. No adhering reaction product was formed on the zinc dust particles. Since activation energies of the products were high (70 kJ/mole for Co and 100 kJ/mole for Ni), the reaction mechanism could not be as simple as reactions shown as Eqs. 2.12, 2.13, and 2.14. It was also found that arsenic was completely removed from the solution before Cu started to precipitate. Therefore, because the arsenic was found only as Cu_3As and CoAs in the precipitate, the actual reaction was probably more likely to be:

$Cu_3As + Co^{+2} + Zn^o = 3\ Cu^o + CoAs + Zn^{+2}$ Eq.2.17.

The activation energy of this type of reaction would be expected to be rather higher. The main cathodic reaction by the galvanic current was reduction of hydrogen ion to hydrogen gas and cobalt is precipitated on copper cathode with arsenic by galvanic action:

$2H^+ + 2e^- = H_2\,(g)$ Eq.2.18.

$2Co^{+2} + 2HAsO_2 + 6H^+ + 10e^- = 2CoAs + 4H_2O$ Eq.2.19.

For the anodic reaction

$Zn^o = Zn^{+2} + 2e^-$ Eq.2.20.

The effect of temperature on cobalt cementation is another concern which was investigated. Lawson and Nhan (14) reported that the reactions for the precipitation of cobalt with arsenic from zinc sulfate solution were:

$2HAsO_2 + 2Co^{+2} + 6H^+ + 5Zn = 2CoAs + 5Zn^{+2} + 4H_2O$ Eq.2.21.

$2HAsO_2 + Co^{+2} + 6H^+ + 4Zn = CoAs_2 + 4Zn^{+2} + 4H_2O$ Eq.2.22.

According to Lawson and Nhans (14) study at different temperatures, above 92°C $CoAs_2$ was formed. Below this temperature CoAs seemed to be the stable product. They also reported that the reaction was limited by a surface chemical step and that reasonable reaction rates were achieved with temperatures in excess of 92°C.

The cementation efficiency was also affected by the particle size of the zinc, as MacKinnon reported (34). It was concluded that the amount of cobalt cemented from solution increases with decreasing particle size of the zinc dust.

It is well known among zinc producers that cemented cobalt tends to redissolve. Oxidation of cemented cobalt by dissolved O_2 is often given as an explanation. Cemented Cu^{+2} and As^{+3} also redissolve (21). Salin (35) explained the redissolution of cobalt by the reaction:

$$Co(s)+Cu^{+2}= Co^{+2} + Cu(s) \qquad \text{Eq.2.23.}$$

West-Sells (36) had proposed that reaction could occur at the cathode surface during electrodeposition of cobalt, when the local pH at the surface is greater than 8:

$$Co(s)+2OH^{-}=Co(OH)_2 + 2e^{-} \qquad \text{Eq.2.24.}$$

Therefore, 1% lead is a common additive to the zinc powder because it increases cobalt cementation kinetics and prevents redissolution of deposited cobalt. Bockman and Ostvold (37) found a relation between the size of the zinc particles and amount of redissolution. In their study they mentioned that the small particles gave a high initial cementation rate, but the redissolution of cobalt was high. The larger particles showed little cementation, but also very little redissolution.

Despite the improvement in kinetics of precipitation of cobalt with activators present, cobalt removal still requires long retention times (3-4 hours), and from time to time the process fails to meet the target level of 0.2 mg/l cobalt in the purified electrolyte, with negative consequences in the electrowinning operation. Even when the target conditions are met, the zinc dust consumption is excessively high, satisfactory operation requires up to 300 times the stoichiometric amount of zinc dust.

The presence of arsenic in the materials used for the extraction of zinc makes precautionary measures imperative. Arsenic hydride gas, commonly called arsine, is an extremely toxic poison. Small amounts breathed into the human system will cause serious illness or even death. Only two conditions are necessary for the formation of arsine: the presence of arsenic and hydrogen. No other condition, such as the presence of acid or metallic is absolutely necessary, although these may be also contributing factors. Positive ventilation and adequate arsine detection and warning system are the best insurance against this hazard in operations where arsine may be encountered. Antimony also forms hydrides although the formation of these elements is not as likely as arsenic. The protective measures taken for arsenic will usually cover the danger from the hydrides of the elements (2).

2.7.4. The Solvent-Extraction Method

At a South African cobalt refinery, cobalt-bearing feed material is leached in sulfuric acid and the resultant liquor is subjected to classical precipitation methods to produce an upgraded cobalt carbonate. This process flow sheet does not allow the flexibility to accept diverse feed materials containing varying quantities of impurity elements such as nickel, manganese, magnesium and zinc, and at the same time satisfy the market requirement for high-purity cobalt products. The development of two solvent-extraction (SX) circuits that were successfully implemented at the operating refinery to overcome these problems is described.

The first SX circuit employs di(2-ethylhexyl)phosphoric acid as the extractant in a pH-controlled circuit to remove contained zinc and manganese. Hydrochloric acid is used as the stripping solution because of the co-extraction of iron and calcium onto the loaded organic phase. A scrub stage is required to minimize the loss of co-extracted cobalt.

In the second circuit, CYANEX®272 is used in pH-controlled extraction and scrub circuits to successfully reject magnesium and nickel in favor of cobalt. Stripping of the loaded organic phase using a sulfuric acid solution is employed to produce a substantially upgraded cobalt sulfate solution from which pure cobalt carbonate is precipitated (38).

Since solvent extraction has been successfully applied to recover and purify cobalt in many industrial applications, the primary requirement of the extractant is to achieve selectivity for cobalt over nickel. To produce high-grade cobalt oxide a cobalt solution essentially free of base metals and low in magnesium is required. Based on the selectivity for cobalt over nickel, magnesium and calcium, the extractant of choice is CYANEX®272.

2.7.5. The Effect of Certain Surfactants on the Cementation of Cobalt from Zinc Sulfate Solutions by Suspended Zinc Particles in the Presence of Copper or Antimony

The effect of surfactants nonylphenolpolyethylene glycol with molecular weight 900 (D1), dinaphthylmethane-4,4'-disulphonic acid (D2) and polyethylene glycol with molecular weight 400 (D3) on both cobalt-zinc dust cementation kinetics and the structure of obtained deposits was investigated in the presence of copper or antimony. The reaction of cobalt cementation was found not to follow first-order kinetics due to the hydrogen evolution which takes place along with cementation reaction. Two rate regions were observed. Surfactants D1 and D3 inhibit but D2 has no effect on cobalt cementation rate. Copper increases but antimony decreases cobalt deposition. On the other hand, the presence of antimony substantially increases the inhibition effect of D1 and D3 on cobalt cementation. A higher temperature improves cobalt cementation.

D1 and D3 inhibit antimony cementation. The effect of D1 is substantially higher and contributes to a large decrease of antimony deposition by zinc dust. The influence of copper and antimony on the structure of obtained deposits is strikingly different. The presence of copper causes the deposition of coarser products containing massive formations of lamellar crystallites. The addition of antimony contributes to the formation of compact uniform layers of deposits with a low porosity on the surface of zinc particles. Surfactants D1 and D3 decrease the crystallite size and deposit porosity and their effect is substantially larger in the presence of antimony. The lowest porosity is found in the presence of both D1 and antimony.

According to the obtained results, the concentration of antimony during the cobalt cementation by zinc dust from the solutions containing surfactants D1 and D3 must be lower than that of copper (39).

2.7.6. Extraction of Cobalt with P507

A hydrometallurgical process has been developed for the recovery of cobalt from a zinc plant residue by Wang and Zhou (40). The residue contains of active carbon and zinc sulfate. In addition, it contains naphthol derivative complexes with cobalt, nickel, iron, copper and other metals. The process consists of the following six major unit operations: (1) washing: 0.5 mol/l sulfuric acid, (2) roasting and leaching: first, roasting at 800°C, then sulfation roasting at 250°C, followed by roasting at 550°C, lixivating with water at 95°C, (3) precipitation of iron and manganese: first at pH 3.5, 95°C, then pH 4-4.5, 95°C, with dropwise addition of 10% ammonium persulfate solution; (4) separation of zinc, cadmium, and copper by anion-exchange resin: 2 mol/l chloride ion, pH 4, where copper was reduced (5) separation of nickel by selective extraction of cobalt: 25% P507 in sulfonated kerosene, pH 4-6, stripping with 3 mol/l hydrochloric acid; (6) precipitation of cobalt. After roasting at 700°C, pure cobalt oxide with cobalt in excess of 74% obtained. The total recovery of cobalt was found to be approximately 94%.

The overall experimental approach used was to leach the cobalt after sulfation roasting, as well as purification of cobalt using different techniques including precipitation, anion-exchange and solvent extraction. The commercial extractant was P507 ((2-ethylexyl) 2-ethylhexyl phosphate, EHEHPA).

The cobalt was precipitated from the strip liquor of the extraction circuit based on the use of P507 as an extractant by addition of excess ammonium oxalate. The consumption of ammonium oxalate was studied. The precipitated cobalt oxalate was filtered, washed with clean water and the filtrate was taken to analyze the concentration of residual cobalt. The oxalate was calcined in a muffle furnace at 700°C to convert the cobalt into oxide.

2.7.7. Cobalt Precipitation by Reduction with Sodium Borohydride

The reduction of cobalt with borohydride is very complicated, as evidenced by the fact that various authors have obtained different reaction stoichiometries and have proposed a number of mechanisms.

The efficiency of cobalt reduction increased with increasing concentration of NaOH in the reducing solution, the best reduction efficiency without the precipitation of cobalt hydroxide being 1 mole of sodium borohydride to reduce 1 mole of cobalt. The reduction efficiency increased with increasing pH, from nil at pH 2 to 96% at pH 6, and decreased with increasing temperature (41).
X-ray diffraction patterns and transition electron microscopy (TEM) patterns of the recovered precipitates showed them to be amorphous.

Zinc ions have a dramatic inhibitory effect on cobalt reduction. Several tens of micromoles per liter zinc ions completely inhibit cobalt reduction with borohydride. The main cause of inhibition is that zinc ions compete with those of cobalt for borohydride ions and zinc borohydride forms and hydrolyzes rapidly.

Sodium borohydride, discovered by Schlesinger in 1942(42), is an efficient, water-soluble reducing agent having the following features:

1. Sodium borohydride has a low equivalent weight of 4.75 g/mol e^- and 1 mole of sodium borohydride can supply 8 moles of electrons;
2. Sodium borohydride has a high reducing power;
3. The sodium borohydride redox reaction can take place in different media, such as water and organic solvents, and under acidic, neutral and alkaline conditions.

These properties distinguish it favorably from other reducing agents. Hence, sodium borohydride has been widely used to reduce a variety of metal cations to the metallic state. These technologies are the basis of several commercial processes, such as the preparation of selective catalysts, the recovery of precious metals from waste water and electroless plating.

Cobalt reduction with sodium borohydride is used to make magnetic materials and catalysts and to remove and recover from wastewater. Cobalt reduction with borohydride is very sensitive to reaction conditions, including: temperature, the method and rate of borohydride addition, pH and the presence of other ions such as zinc and copper. The stoichiometry and reaction mechanism are still unclear.

Polyakov et. al. (43) reported that 1.1 moles of sodium borohydride can reduce 4 moles of cobalt ions to lower the concentration of cobalt ions in zinc sulfate electrolyte to 0.01 ppm in the presence of triethanolamine. However, Awadalla et. al. (44) reported that 2 moles of sodium borohydride can only reduce 1 mole of cobalt ions and that zinc ions have a strong negative effect on cobalt reduction. Studies by Cominco Ltd. have shown that borohydride can not reduce cobalt from zinc sulfate solution in the purification step prior to zinc electrowinning.

In view of the conflicting data, it was decided that a careful study of cobalt reduction with sodium borohydride should be conducted to clarify the chemistry of the process and to see if borohydride reduction might be a feasible alternative for the removal of cobalt in zinc electrolyte purification.

2.7.8. Cobalt Cementation with Ferromanganese

DeBecker et. al. (45) have shown that copper and zinc are readily cemented on manganese powder at room temperature. They showed that under the same conditions, the cementation of cobalt is slower and incomplete. It is worth noting that the cementation of cobalt with zinc powder is difficult in a zinc-rich electrolyte at low temperature because of slow reaction rate and low efficiency.

For cementation two ferromanganese alloys have been investigated by Yang et. al. (46); standard ferromanganese (6.8% carbon) and medium carbon ferromanganese (1.4% carbon). The rate is measured by rotating-disk experiments and the results show that cobalt cementation on the ferromanganese is a first-order reaction controlled by mass transfer. Tests are carried out at room temperature. The reaction is fast in the pure sulfate solution and the efficiency of use of manganese is close to 100%. Cementation of cobalt with ferromanganese does not proceed to a significant level in mixed cobalt and zinc-sulfate solution.

2.7.9. Oxidation-Precipitation of Cobalt from Sulfate Solution using Caro's Acid

A process utilizing Caro's acid to precipitate cobalt from Zn-Cd-Co-Ni sulfate solution was investigated by Owusu (47). Caro's acid oxidizes Co(II) to Co(III) species. About 98-99% of the cobalt contained in the feed solution was precipitated as $Co(OH)_3$ at pH 3.5-4.0. However, at pH≤2.5, less than 8% of the cobalt present in the feed was precipitated. At such low pH's, a dark green colloidal suspension was generated and this was difficult to filter. Results obtained from both batch and continuous experiments were similar. The cobalt content of the $Co(OH)_3$ precipitate was 47-49% which is fairly close to the theoretical value of 53.6%. The impurities consisted of 3-4% Zn, about 1% Cd and less than 0.005%Ni.

In the oxidation-precipitation of cobalt, Co(II) ionic species are oxidized to the Co(III) state which precipitates out of the solution as an insoluble cobaltic hydroxide, $Co(OH)_3$ (or $Co_2O_3.3H_2O$). Oxidation-precipitation reactions require the use of a powerful oxidant. One such oxidant is Caro's acid. It has been used as an oxidant: for acid leaching of uranium ores, to oxidize vanadium (IV) to vanadium (V) prior to solvent extraction. Caro's acid is prepared by the direct addition of hydrogen peroxide to concentrated sulfuric acid with cooling to remove the heat of reaction.

2.7.10. Manganese Dust Purification

Manganese and zinc powders were used as cementation agents in the study by Blaser (26). Little previous information exists on the use of manganese as a cementing agent and it is of interest for several reasons. Manganese has a more negative reduction potential than zinc and could, therefore, provide a larger driving force for the cementation reactions; since manganese will cement zinc, the freshly deposited, finely divided zinc could enhance removal of impurities. Two experiments were made under the same conditions; the only variable was the cementing agent. One of them, was zinc dust, the other was manganese dust. As a result, it was indicated that the Mn is slightly more effective than Zn in removing Co from solution, all other factors being comparable.

2.7.11. New Type Zinc Powder Purification

A new-type zinc powder containing traces of tin was investigated by Qing-heng et. al.(48) in 1985 as an additive to see if it could be used to replace arsenic for cobalt cementation. By use of the new-type of zinc powder bearing tin equaling 1.5-2.5 times the amount of cobalt in the solution, it is possible at 65-75^{o}C to reduce the Co content of a $ZnSO_4$ solution containing 70 mg/l Cu^{+2} to traces or to a predetermined amount within 20-45 minutes. The cobalt content could be reduced to 1 or 0.2 mg/l.

X-ray diffraction diagrams showed that zinc was the predominant phase in the purification residue, with other phases of Cu_xSn_y, Co_xSn_y and $Co_xCu_ySn_z$ being present in small traces. On rare occasions a separate tin phase was detected. But neither cobalt or copper phase, nor a Co_xZn_y phase could be found separately. It was therefore concluded that cobalt cementation did not occur on zinc, but on the surfaces of zinc particles containing tin or copper-tin activated spots.

The use of the new type of zinc powder for cobalt cementation was recommendable because it caused no environmental pollution, imposed no danger onto the health of operating workers, and allowed a cut in power consumption at the following steps. It was also preferable because it was easy to prepare the alloy and possible to be stored in atmospheric conditions for long periods.

On an increased content of tin in the new-type zinc powder there was a decrease in the amount of cobalt remaining in the solution. This is because that increasing within limits the tin content in the zinc powder gives rise to more activated spots on the zinc particles, thus preventing hydrogen ions from giving up their charges and assisting in the precipitation of Co^{+2}, i.e., the reaction is accelerated. For this study, two different tin-zinc alloys containing 4%Sn and 10%Sn were prepared. The phase diagram of the system is given in Figure 2.12.

After the study of Qing-heng, Nelson et. al.(25) worked on finding new additives for cobalt removal from zinc electrolyte. Among novel activators tested by Nelson, tin was equally as effective as antimony in removing cobalt. The initial kinetics of cobalt cementation with tin were faster than with antimony. This could shorten the necessary residence time for the process.

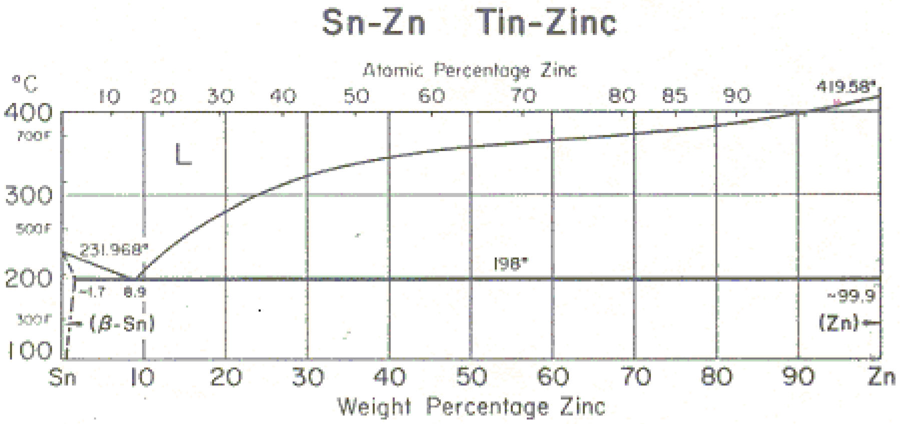

Figure 2.12. The Phase Diagram of Sn-Zn Alloy (49)

2.7.12. Molecular Recognition Technology for Cobalt Removal

The use of "Molecular Recognition Technology" (MRT), a highly selective separation technology using specifically designed ligands, has been demonstrated to be an effective treatment process for removal of several ions that are commonly found in many hydrometallurgical circuits as well as in environmental treatment operations. Ions removed by MRT include base, heavy and transition metals, precious metals, halides, and alkali/alkaline earths. MRT provides rapid, selective extraction and recovery of cations and anions from process or waste streams and enables commercial metallurgical separations to enhance processes that were previously not technically or economically feasible (50).

A MRT pilot plant run was conducted at Zincor (South Africa) to demonstrate the cobalt/nickel purification of zinc electrolyte, and to recover saleable pure cobalt/nickel sulfate solution. The MRT process holds various advantages, which include the elimination of a catalyst such as arsenic trioxide, conventionally used in cobalt and nickel cementation. SuperLig® 138 can be used to remove cobalt and nickel from 120-170 g/l Zn-solutions at pH 1-2. The Zincor MRT application demonstrated its capability of concentrating large volumes of copper barren impure solution at low cobalt and nickel concentration levels in the feed, to small solution volumes at high cobalt and nickel concentrations. Around 99.5% of the cobalt was removed from solution with cobalt impurity levels in feed varying between 10 mg/1 and 26 mg/l.

MRT represents a significant advance over ion exchange systems in that it is a highly selective system using specially designed ligands. These ligands are chemically bonded to solid supports such as silica gel or polymers or used free in solution to complex with selected ions. This is often accomplished without an exchange of ions.

The product, SuperLig® 138 binds both Co(II) and Co(III). However, SuperLig® 138 binds Co(III) stronger and with greater selectivity over other elements/ions which have trace affinity for SuperLig® 138. Experimental tests with highly concentrated zinc solutions have shown that Co is only polished to trace or below detection levels from such solutions, bound as Co(III).

The MRT process holds various advantages for copper and cobalt separations**.** For cobalt removal at Zincor, advantages would include:

1. The elimination of arsenic trioxide (which is a potential environmental and health hazard)
2. Reduction of zinc recycles
3. No generation of an arsenic containing by-product
4. The generation of a high-quality cobalt and nickel product which can be sent for toll refining or cobalt electrowinning
5. Simplification of the zinc circuit
6. Improvement in cobalt recovery
7. Reduction in the solution cobalt content to extremely low levels.

2.7.13. Xanthate Purification

It is well known that soluble xanthate compounds form metallic xanthate precipitates when they come into contact with metallic salts (6). Cobalt can also be removed from solution by the addition of an aqueous solution of sodium ethyl xanthate, if used in conjunction with an oxidizing agent such as potassium permanganate or copper sulfate. Copper takes part in the reaction and should be present. Zinc xanthate is first formed which, when copper is used, reacts to form cuprous xanthogenate, and the oxidizing process is transferred to the cobaltous salt to form insoluble cobaltic xanthogenate. Efficiency of the purification is improved if cadmium is first reduced to small amounts (51).

2.8. Purification Methods of Operating Zinc Smelters and Refineries in the World

According to Yamada (6) 77% of hydrometallurgical plants that replied to his questionnaire adopted continuous purification system, and 66% of them use 2-stage purifying step. In regard to the additives for cobalt removal, both antimony and arsenic oxide were almost equally used to activate zinc dust purification, and these two activators covered over 80% of the total kinds of additives. However, concerning the addition of additives, antimony oxide was far less than arsenic oxide as shown in Figure 2.13.

In comparison of cobalt concentration in leach solution, antimony oxide was used at an average level of 13.4 mg/l Co, while arsenic oxide at an average level 24.5 mg/l Co. Therefore, the arsenic oxide addition seems to be suitable for higher cobalt loading.

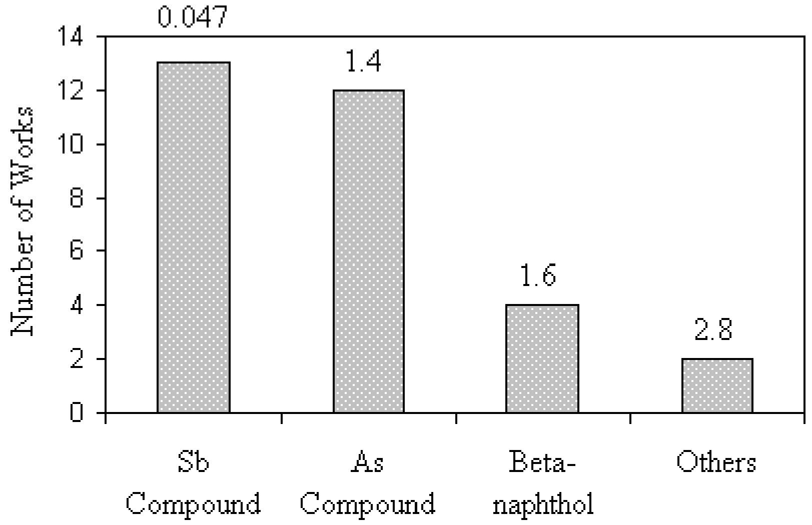

Figure 2.13. Additives used for Cobalt Removal (Additive amounts in figure are given as kg/ton of zinc produced)

CHAPTER 3

EXPERIMENTAL SET-UP AND PROCEDURE

3.1. Introduction

Çinkur is the only electrolytic zinc plant in Turkey. It has a capacity of 40,000 ton/year electrolytic zinc metal. In the past, it processed carbonate type zinc ores mined in the region of Kayseri. After its privatization in 1997, the new owners being Iranian decided to process imported Iranian concentrate only at Çinkur. The zinc plant was closed down about 3 years ago and the production of zinc was stopped.

Since the Turkish ores were low in cobalt, the pregnant leach solution obtained by leaching of these ores, had less than 10 mg/l cobalt, the purification of which was not a serious problem. With the closure of the Waelz kilns and the use of Iranian zinc concentrate only in direct leaching, the amount of cobalt in pregnant leach solution increased to 50-100 mg/l which created serious problems in purification and the in following zinc electrowinning step. This problem originated from the higher cobalt content of the imported Iranian zinc concentrate.

Iran has a number of lead-zinc mines, of which the Argouran mine near Zanjan in northwestern Iran is the largest in the Middle East. It is controlled by the State of Iran. Here, a new 40,000 ton/year lead smelter has come into production in recent years and a 60,000 ton/year zinc smelter is scheduled to be built. Iran's total production of lead-zinc ores is estimated to be about 2 million ton/year, from which 168,000 tons concentrates are produced (52). Some of the carbonate type zinc concentrate was imported to Çinkur after calcination in Iran for processing.

3.2. Preparation of Synthetic Leach Solutions

Cobalt cementation experiments were done in this study. The studies were carried out by using synthetic leach solutions. Stock synthetic solutions of 1 l or 2 l in volume were prepared for the experiments. For the stock solution to represent the pregnant leach solution at Çinkur A.Ş., the solution should contain approximately 150 g/l zinc and 75 mg/l cobalt. The amounts of zinc and cobalt mentioned above were added in the form of Merck quality pure zinc sulfate $ZnSO_4.7H_2O$ and pure cobalt sulfate $CoSO_4.7H_2O$. All synthetic solutions were prepared with the use of de-ionized water. The chemical analyses of the stock solutions were checked after their preparation and with time. It was seen that the metal concentration levels remained constant with time and the pH of the solutions was around 4.0.

3.3. Preparation of Zinc Powders

In this research, a new-type of zinc powder containing tin was investigated as an additive to see if it could be used to replace arsenic trioxide totally or in part for cobalt cementation. Two different powders were prepared; one of them containing 4.0% Sn and the other one containing 10% Sn. The tin containing zinc powder was prepared by melting electrolytic zinc metal obtained from Çinkur in an induction furnace. Then, the calculated amount of pure tin was added to the molten zinc and pulverized by blowing air at powder metallurgy laboratory of the Metallurgical and Materials Engineering Department. These powders were –208 microns (65 Tyler mesh) in size.

For the precipitation of cobalt from the synthetic leach solution either pure zinc (99.99% Zn) with a particle size of -208 microns used at Çinkur or one of the prepared powders containing tin was used. The powders were cleaned before use with 10 g/l sulfuric acid to get rid of the oxide layer that was present on zinc powders.

3.4. Experimental Set-up Used and the Procedure of Cementation

The cementation experiments were conducted at the desired temperature using a Velp Arex 2 model hot plate with magnetic stirrer and a 250 cc Pyrex balloon with three necks. The temperature was controlled by a contact thermometer within an accuracy of $\pm 2^{o}C$. In the experiments, the stirring speed was kept constant by setting the stirrer speed at a certain setting in order to obtain sufficient mixing of solids with the liquid phase. A water-cooled condenser was attached to the central opening of the balloon in order to prevent solution loss by evaporation. A representative diagram of the experimental set-up is shown in Figure 3.1.

In each experiment, a measured quantity of synthetic solution which was usually 250 cc, was placed into the Pyrex balloon and heated to the desired temperature. Then, pure copper sulfate of Merck quality in the form of $CuSO_4.5H_2O$ crystals and Riedel-de Haen quality arsenic trioxide (As_2O_3) in pure solid form, were added into the solution in calculated amounts, respectively. After the dissolution of arsenic trioxide in the synthetic solution, finally pure zinc or tin containing zinc powder was added. After this addition, the experimental duration was started. At the end of each cementation experiment without letting the temperature to drop, the contents of the balloon were filtered through a filter paper using a Buhner funnel. So the hot solution was separated from cementate by filtration. Water washed and dried cementates were stocked for the XRD and SEM investigations. The filtrates were analyzed by Perkin Elmer model 2380 type Atomic Absorption Spectrophotometer (AAS) for cobalt. Special precautions were taken in AAS analysis in order to prevent the interference of high amount of zinc present in filtrate in cobalt analysis.

The cementation efficiency for each experiment was calculated from the analysis of the initial and final concentrations of cobalt in the solution.

This study focused on optimizing as many operating parameters as possible that affects the cobalt cementation process. The variables in the experiments were identified as arsenic trioxide, copper sulfate, zinc or zinc-tin alloy powder amounts added into the solution, experiment duration, and temperature.

At the first stage, the experiments with pure zinc powder were conducted. Arsenic trioxide optimization with zinc powder was done. In these experiments, different amounts of arsenic trioxide were added into the solution, whereas the amounts of zinc powder and copper sulfate additions were kept constant. Then, a series of experiments were done to investigate the effect of varying amounts of copper sulfate addition.

At the second stage, the experiments were conducted with 4.0%Sn-Zn alloy powder. The optimization of arsenic trioxide, copper sulfate and tin containing zinc alloy powder amounts were done.

At the third stage, the experiments were conducted with 10%Sn-Zn alloy powder. The first parameter investigated was 10%Sn-Zn powder amount. The other parameters were tried to be optimized after this investigation. Parameters of temperature and time were also tried to be optimized in both of the zinc alloy experiments.

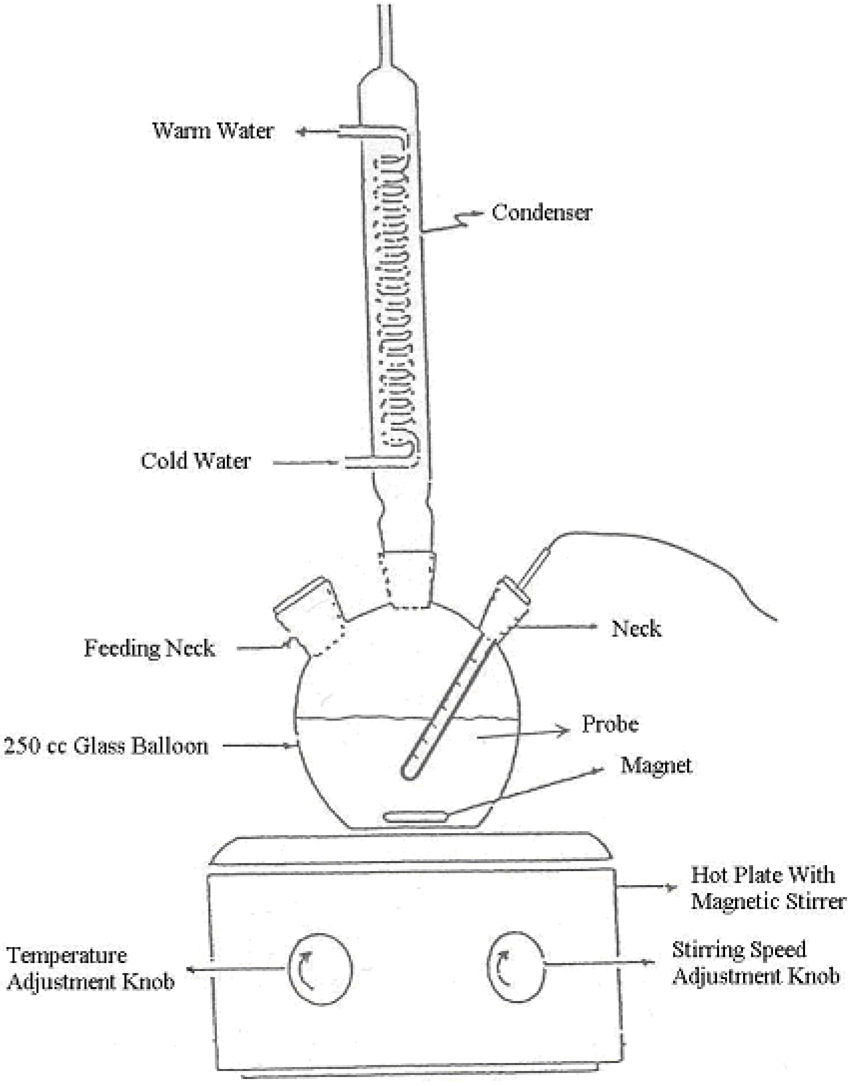

Figure 3.1. Schematical Drawing of Experimental Set-up

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Introduction

In this study several tests were performed looking at different parameters influencing the cobalt cementation from synthetic zinc electrolyte. These parameters were: the effect of amount of As_2O_3, amount of copper sulfate, amount of zinc alloy powder (dust), temperature and duration.

The aim of this study was to investigate a new additive, namely tin containing zinc alloys for cobalt cementation with or without the use of As_2O_3. Initially, a few experiments were conducted with pure zinc powder with the other additives used in conventional methods for comparison purposes. In these experiments, two major factors were taken into consideration; amount of arsenic trioxide and amount of copper sulfate. The rest of the parameters were not studied, as there are many works about them in the literature. On the other hand, in the presence of tin containing zinc alloy powders of two different compositions, all of the parameters were studied in order to determine the effect of each variable on cobalt cementation.

4.2. Cementation with Pure Zinc Powder

4.2.1. Effect of the Amount of As_2O_3 Additions on Cobalt Cementation

The first parameter investigated was the effect of the amount of solid arsenic trioxide added to the synthetic pregnant leach solution on cobalt cementation. In the experiments, the amount of As_2O_3 added was varied between 0 and 0.20 g/l. In all of the experiments related to arsenic trioxide, the other variables were kept constant as follows: $CuSO_4.5H_2O$ added 0.4 g/l, precipitation temperature of 85^{o}C, precipitation duration of 2 hours, amount of pure zinc powder added 4.0 g/l.

As it can be seen from Table 4.1 and Figure 4.1, without any arsenic addition, the amount of cobalt precipitation was only 8.72%. So without an addition of an activating agent such as arsenic trioxide, the cobalt precipitation was very limited. With the addition of increasing amount of arsenic trioxide, the amount of precipitated Co increased up to a maximum of 78.72% and then decreased with the excessive addition of the activator. This kind of detrimental effect of excessive additions of an activator such as antimony trioxide was also reported by Tozawa (6). Although no explanation could be found in the literature for this drop, it might be due to the prevention of precipitation of CoAs on zinc powder or Cu_3As that formed on zinc powder. As a result, the optimum amount of arsenic was determined as 0.12 g/l. In the experiments, the initial pH of the synthetic leach solution was 4.0 ± 0.1. After cementation, the final pH values of the purified solutions were 5.0 ± 0.1. So the pH of the solution was allowed to reach its own equilibrium without making any adjustments.

Table 4.1. Results of Cobalt Precipitation with Varying Arsenic Trioxide Addition using Pure Zinc Powder

Exp. No	Amount of As_2O_3 Added (g/l)	Amount of Zinc Dust Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (°C)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
1	0	4	0.4	2	85	75.2	68.6	8.72
2	0.06	4	0.4	2	85	75.2	36.6	51.33
3	0.10	4	0.4	2	85	75.2	24.2	67.82
4	0.12	4	0.4	2	85	75.2	16.0	78.72
5	0.16	4	0.4	2	85	75.2	22.0	70.74
6	0.18	4	0.4	2	85	75.2	27.0	64.09
7	0.20	4	0.4	2	85	75.2	29.3	61.03

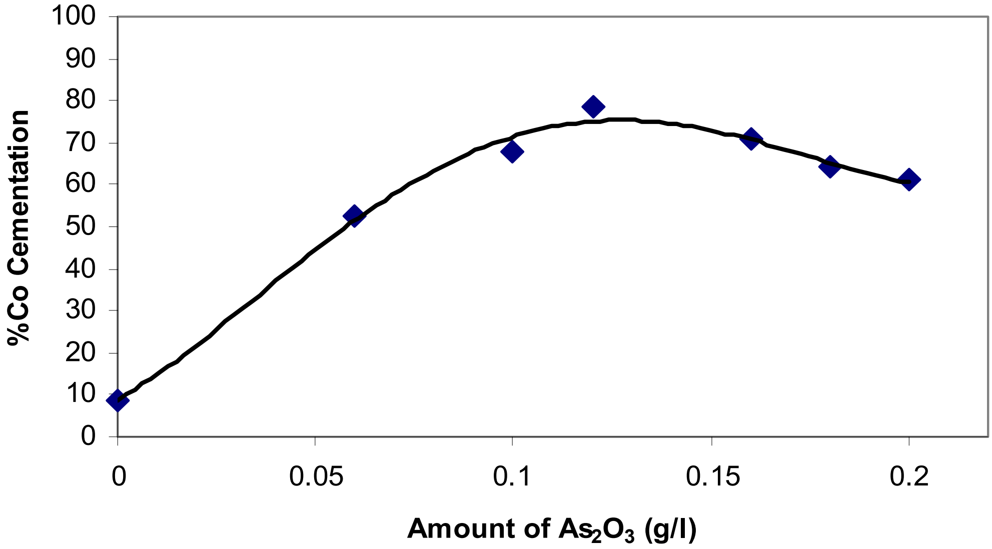

Figure 4.1. The Effect of Amount of As_2O_3 Added on Cobalt Cementation using Pure Zinc Powder

4.2.2. Effect of the Amount of Copper Sulfate Additions on Cobalt Cementation

The second parameter that was investigated with the use of pure zinc as the cementing agent was the effect of the amount of copper sulfate added to the leach solution in the form of $CuSO_4.5H_2O$ on cobalt cementation. The other variables were kept constant as: 0.12 g/l As_2O_3, 85°C precipitation temperature, 2 hours precipitation duration and 4.0 g/l pure zinc powder.

Without any copper ion addition, the cobalt precipitation was 69.84%. The cementation of cobalt increased with the increasing addition of copper sulfate. This is due to the fact that copper forms a larger cathodic surface for cobalt deposition and creates small galvanic cells that are suitable for cobalt deposition (37). So, small amount of copper addition was found to be beneficial for cementation of cobalt as seen from Table 4.2.

Fugleberg has recommended that small additions of copper ions should be made, which was stated as beneficial for cobalt precipitation (33). It is generally thought that copper ions form Cu_3As as a substrate on the surface of the zinc powder, which acts as an active site for the precipitation CoAs.

Table 4.2. Results of Cobalt Cementation with Varying Copper Sulfate Addition using Pure Zinc Powder

Exp No	Amount of As_2O_3 Added (g/l)	Amount of Zinc Dust Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Duration Of Exp. (hr)	Temp. of Exp. (°C)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
8	0.12	4	0	2	85	75.2	22.7	69.84
4	0.12	4	0.4	2	85	75.2	16.0	78.72

4.3. Cementation with Tin Containing Zinc Alloy Powders

Two sets of experiments were conducted by using two different zinc-tin alloy powders. One of them contained 4% tin and the second one had 10% tin on the other hand.

4.3.1. Cementation with 4.0% Sn-Zn Alloy Powder

The first series of experiments for cobalt cementation with zinc-tin alloy involved the use of 4% Sn containing zinc alloy powder.

4.3.1.1. Effect of the Amount of As_2O_3 Additions on Cobalt Cementation

The first parameter investigated was the effect of the amount of solid arsenic trioxide added to the synthetic pregnant leach solution on cobalt cementation. In the experiments, the amount of As_2O_3 added was varied between 0 and 0.22 g/l. In all of the experiments related to arsenic trioxide, the other variables were kept constant as follows: $CuSO_4.5H_2O$ added 0.4 g/l, precipitation temperature of 85°C, precipitation duration of 2 hours, amount of zinc alloy powder added 4.0 g/l.

As it can be seen from Table 4.3 and Figure 4.2, the precipitation behavior of cobalt was similar to that observed in the experiments done with the conventional method using pure zinc powder. Without any arsenic addition, the amount of cobalt precipitated was 37.50%. So without an activating agent, precipitation of cobalt with 4.0% Sn-zinc alloy powder was not very effective. With the addition of increasing amounts of arsenic trioxide, the amount of Co precipitated increased up to a maximum of 91.37% and then decreased with the excessive additions of the activator. As a result, the optimum was taken as 0.12 g/l As_2O_3. As it can be seen from Tables 4.1 and 4.3 that, higher cobalt cementations were obtainable with the use of 4.0% Sn -zinc alloy powder rather than pure zinc powder. In all of the experiments, the initial pH of the synthetic leach solution was 4.0 ± 0.1. After cementation, the final pH values of the purified solutions were 5.0 ± 0.1. So the pH of the solution was allowed to reach its own equilibrium without making any adjustments.

Table 4.3. Results of Cobalt Cementation with Varying Arsenic Trioxide Addition using 4.0% Sn-Zn Alloy

Exp. No.	Amount of As_2O_3 Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Amount of %4 Sn-Zn Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (^oC)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
9	0.00	0.4	4	2	85	75.2	47.0	37.50
10	0.04	0.4	4	2	85	75.2	26.6	64.63
11	0.06	0.4	4	2	85	75.2	25.6	65.96
12	0.08	0.4	4	2	85	75.2	23.8	68.35
13	0.10	0.4	4	2	85	75.2	11.0	85.37
14	0.12	0.4	4	2	85	75.2	6.50	91.37
15	0.14	0.4	4	2	85	75.2	11.7	84.47
16	0.16	0.4	4	2	85	75.2	9.88	86.86
17	0.18	0.4	4	2	85	75.2	9.07	87.93
18	0.20	0.4	4	2	85	75.2	13.2	82.45
19	0.22	0.4	4	2	85	75.2	15.6	79.25

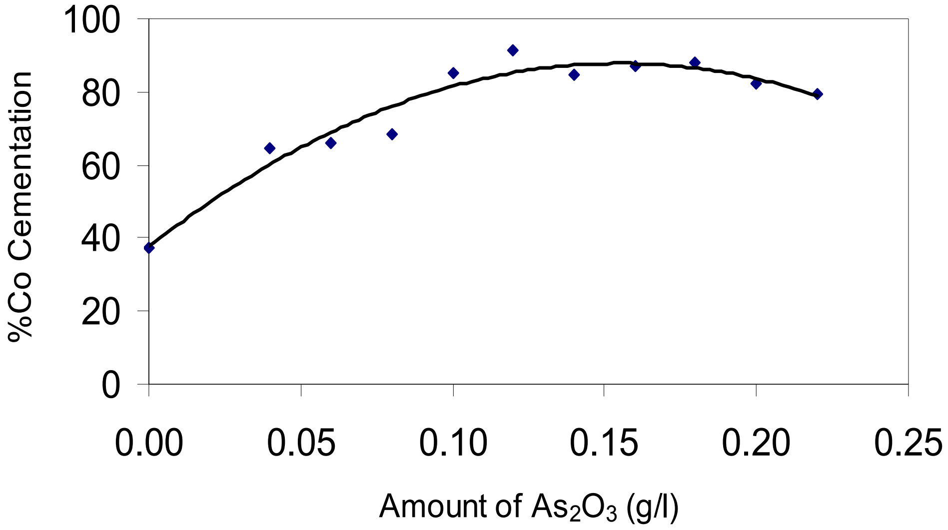

Figure 4.2. The effect of As_2O_3 Addition on Cobalt Cementation using 4.0% Sn-Zn Alloy

4.3.1.2. Effect of the Amount of Copper Sulfate Additions on Cobalt Cementation

The second parameter investigated with the use of 4.0% Sn-zinc alloy was the effect of the amount of copper sulfate added to the leach solution in the form of $CuSO_4.5H_2O$ on cobalt cementation. The amount of added copper sulfate was varied between 0 and 4 g/l. The other variables were kept constant as: 0.12 g/l As_2O_3, 85°C precipitation temperature, 2 hours precipitation duration and 4.0 g/l zinc alloy powder.

Without any copper ion addition, the cobalt precipitation was not more than %19.95. The cementation of cobalt drastically increased with the addition of copper sulfate as seen in Table 4.4 and Figure 4.3. Only 0.4 g/l copper sulfate addition increased the cobalt cementation from %19.95 to %91.37. This may be due to the fact that copper forms a larger cathodic surface for cobalt deposition. Between 0.4 g/l and 1.2 g/l copper sulfate additions, the cobalt cementation efficiency increased slowly from 91.37% to 96.73%. Beyond this amount, with the addition of excessive copper, the cobalt cementation started to decrease. So, limited amount of copper addition was found to be essential for cementation of cobalt. Similar finding was found with the addition of pure zinc instead of an alloy but the cobalt cementation results were much better with the use of alloy.

As a result of these experiments, 1.2 g/l of $CuSO_4.5H_2O$ addition was taken as the optimum amount, as the maximum precipitation of cobalt which corresponded to 96.73%, occurred with the addition of this amount. The reproducibility of experimental results and chemical analysis were also good as seen from Table 4.4.

After the optimization of copper addition was done, two experiments were done with less amount of arsenic trioxide while keeping the other variables constant. One of them contained 0.04 g/l and the other one contained 0.06 g/l As_2O_3. The cementation efficiencies of cobalt, which were 91.01% and 92.04%, respectively, were not as high as the result obtained with the use of 0.12 g/l As_2O_3.

Table 4.4. Results of Cobalt Cementation with Varying Copper Sulfate Addition using 4.0%Sn-Zn Alloy

Exp. No.	Amount of As_2O_3 Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Amount of %4 Sn-Zn Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (^oC)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
20	0.12	0	4	2	85	75.2	62.2	17.29
21	0.12	0	4	2	85	75.2	60.4	19.68
21	0.12	0	4	2	85	75.2	60.2	19.95
14	0.12	0.4	4	2	85	75.2	6.50	91.37
22	0.12	0.8	4	2	85	75.2	4.66	93.80
23	0.12	1.2	4	2	85	75.2	2.46	96.73
24	0.12	1.6	4	2	85	75.2	2.74	96.35
25	0.12	2	4	2	85	75.2	2.80	96.28
26	0.12	3	4	2	85	75.2	4.10	94.55
27	0.12	4	4	2	85	75.2	6.32	91.59

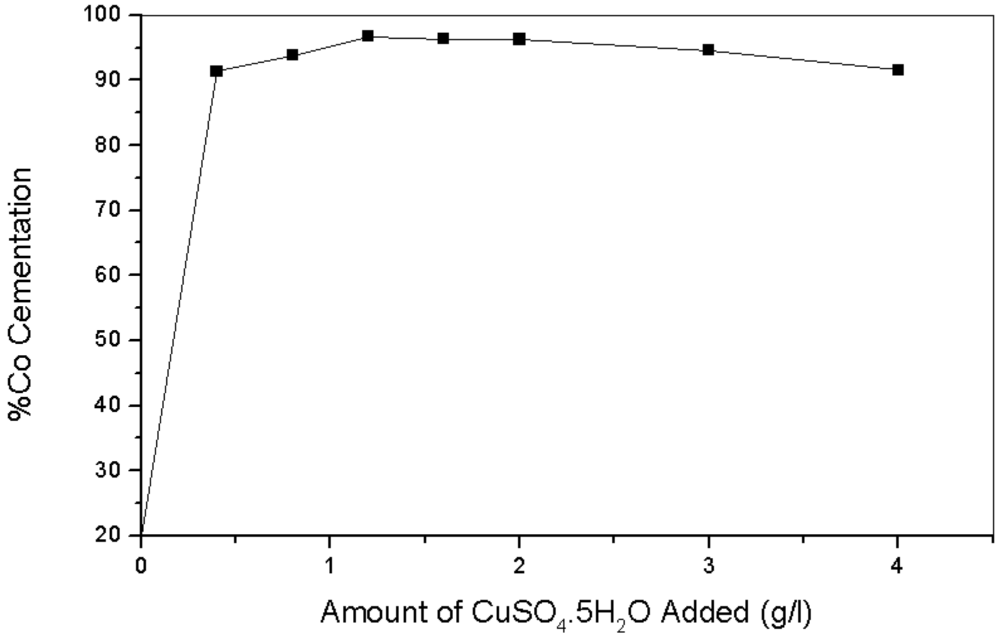

Figure 4.3. The Effect of Copper Sulfate Addition on Cobalt Recovery using 4.0% Sn-Zn Alloy

4.3.1.3. Effect of the Amount of %4.0 Sn-Zn Powder Additions on Cobalt Cementation

The third investigated parameter was the effect of amount of 4.0% Sn-Zn alloy powder addition. The other variables were kept constant in these experiments as follows: 0.12 g/l As_2O_3, 1.2 g/l $CuSO_4.5H_2O$, 85°C cementation temperature and 2 hours cementation duration.

As seen from Table 4.5 and Figure 4.4, the amount of precipitated cobalt increased as the amount of zinc alloy addition increased up to 8 g/l zinc. The cobalt cementation efficiency was %99.19 at this point. This was due to the fact that, the higher the ratio of the active surface area of the cementing metal to the volume of solution, the more efficient was the precipitation. Beyond this amount, the cementation of cobalt did not vary considerably. Slight decreases that might be observed in the cementation of cobalt as seen in Table 4.5, could be due to passivation of the zinc alloy powder due to the formation of basic zinc sulfate on its surface which prevented cobalt precipitation at excessive zinc alloy powder additions as stated in the literature (33). It was found that 8 g/l zinc alloy dust was sufficient to bring the level of cobalt to less than 1 ppm under the optimum conditions. But such a high consumption of the alloy powder would not be economical in an industrial operation.

In industry pure zinc dust consumption may be equal up to 3-8% of the cathodic zinc production (53). The average consumption of pure zinc dust for the purification of zinc leaching solution is not usually more than 25 kg per ton of electrolytic zinc, which is equivalent to about 4 g/l zinc powder.

So if the level of cobalt remaining in the purified solution is decided to be higher than 1 ppm in order to prevent the excessive amount of zinc alloy dust consumption, 4 g/l zinc alloy dust can be chosen as the sufficient amount. Then, the cobalt level of the purified solution will be about 2 ppm for an initial Sn/Co weight ratio of 2.12:1. In fact, at Çinkur with the use of 26.0-40.0 kg pure zinc powder per ton of electrolytic zinc, the typical cobalt levels of the purified leach solution was about 2 ppm.

Table 4.5. Results of Cobalt Cementation with Varying 4.0% Sn-Zn Alloy Powder Addition

Exp. No	Amount of As_2O_3 Added (g/l)	Amount of %4 Sn-Zn Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (^oC)	Sn/Co Ratio By Weight	*Co Final (ppm)	%Co Cementation
30	0.12	2	1.2	2	85	1.06/1	29.8	60.30
23	0.12	4	1.2	2	85	2.12/1	2.35	96.73
31	0.12	6	1.2	2	85	3.18/1	3.07	95.92
32	0.12	8	1.2	2	85	4.24/1	0.61	99.19
33	0.12	10	1.2	2	85	5.30/1	0.72	99.04
34	0.12	12	1.2	2	85	6.36/1	0.73	99.03

* Initial cobalt concentration was 75.2 ppm

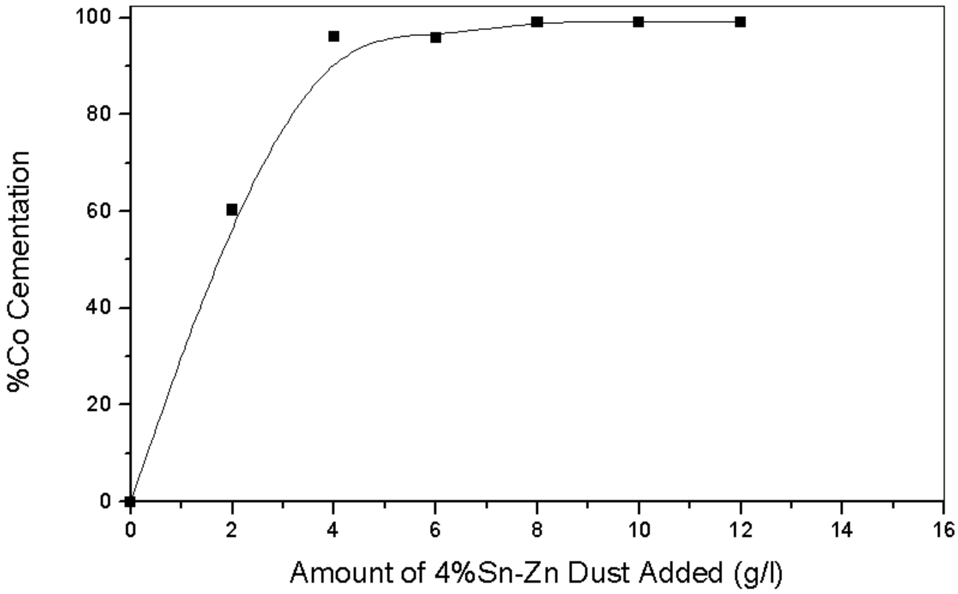

Figure 4.4. The Effect of Amount of 4.0% Sn-Zn Alloy Dust Addition on Cobalt Cementation

4.3.1.4. Effect of Cementation Duration on Cobalt Cementation

The next parameter investigated with the prepared alloy was the effect of cementation duration on cobalt recovery. The experiments were carried out by changing the duration between 1 hour and 5 hours. The other variables kept constant as in the investigation of the other parameters were as follows: 0.12 g/l As_2O_3, 1.2 g/l $CuSO_4.5H_2O$ and 4 g/l zinc alloy dust, 85°C cementation temperature.

It is clear from Table 4.6 and Figure 4.5 that, there was an increase in the amount of cobalt cementation up to 2 hours. Beyond 2 hours there was a little decrease in the cementation efficiency. This little drop could be due to the reversion of the reaction due to redissolution of the cementate. So, the optimum cementation duration was taken as 2 hours.

Table 4.6. Results of Cobalt Cementation with Duration using 4.0% Sn-Zn Alloy

Exp. No.	Amount of As_2O_3 Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Amount of %4 Sn-Zn Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (^oC)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
35	0.12	1.2	4	1	85	75.2	20.5	72.74
26	0.12	1.2	4	1.5	85	75.2	5.60	92.55
23	0.12	1.2	4	2	85	75.2	2.35	96.73
36	0.12	1.2	4	3	85	75.2	2.90	96.14
37	0.12	1.2	4	5	85	75.2	2.80	96.28

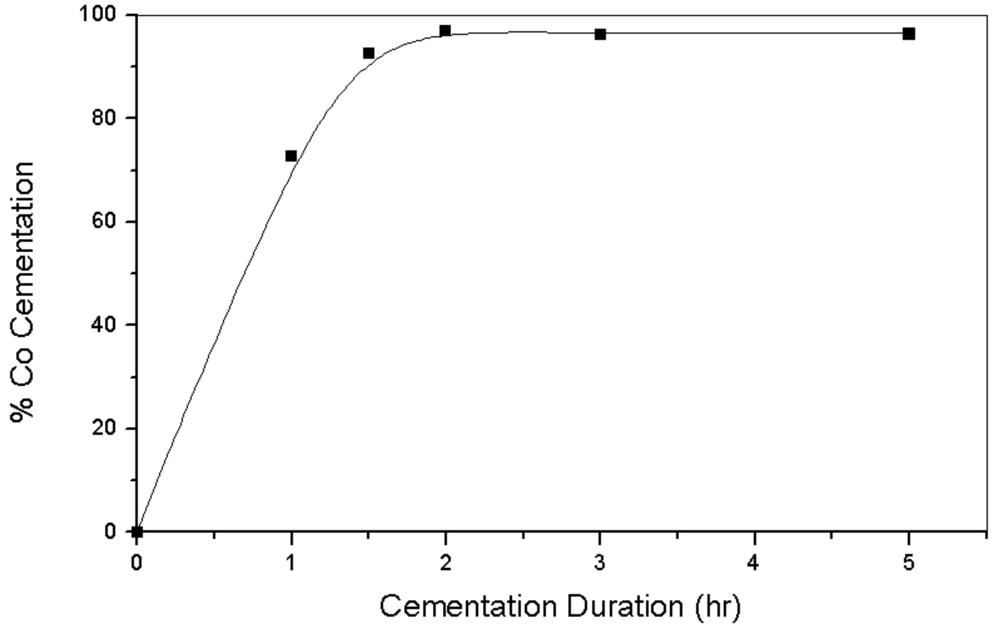

Figure 4.5. The Effect of Cementation Duration on Cobalt Cementation using 4.0% Sn-Zn Alloy Dust

4.3.1.5. Effect of Cementation Temperature on Cobalt Cementation

It's well known that cobalt cementation is affected by the reaction temperature, so the last parameter investigated was the effect of temperature on cobalt cementation. The temperature was varied between 25°C and 90°C. The other experimental conditions were kept constant.

From an industrial point of view, a low temperature of cementation is beneficial not only because it decreases energy consumption in the purification stage, but also it decreases the amount of cooling of the electrolyte to about 40°C that is necessary before electrowinning.

In spite of the advantages of a low temperature of cementation mentioned above, it can be seen from Table 4.7 and Figure 4.6 that, the increasing temperature resulted in an increase in the amount of cobalt cemented. It is clear that the increasing of temperature favors the cementation of cobalt. At 25°C the cobalt cementation efficiency was only 18.62%. With an increase of temperature to 90°C, the cementation of cobalt reaching up to 97.27% was possible. So, the higher is the temperature, the higher is cementation efficiency of cobalt. As a result, the cementation temperature of 85-90°C was decided to be the optimum temperature range.

Table 4.7. Results of Cobalt Cementation with Temperature using 4.0% Sn-Zn Alloy

Exp. No.	Amount of As_2O_3 Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Amount of %4 Sn-Zn Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (°C)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
38	0.12	1.2	4	2	25	75.2	61.2	18.62
39	0.12	1.2	4	2	40	75.2	49.6	34.04
40	0.12	1.2	4	2	60	75.2	36.2	51.86
23	0.12	1.2	4	2	85	75.2	2.46	96.73
41	0.12	1.2	4	2	90	75.2	2.05	97.27

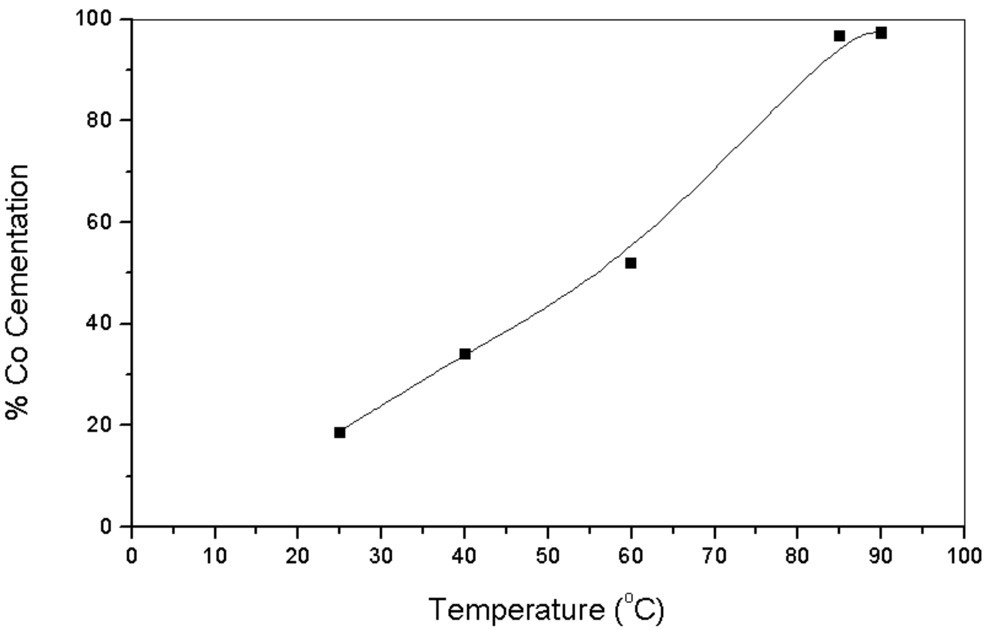

Figure 4.6. The Effect of Temperature on Cobalt Cementation using 4.0% Sn-Zn Alloy

4.3.2. Cementation with 10%Sn-Zn Alloy Powder

The second series of experiments for cobalt cementation with zinc-tin alloy involved the use of 10% Sn containing zinc alloy powder.

4.3.2.1. Effect of the Amount of Zinc Alloy Dust Addition on Cobalt Cementation

The effect of the amount of 10%Sn-Zn alloy powder added was investigated first on cobalt cementation. The amount of added zinc alloy dust was varied between 2 g/l and 16 g/l. As the aim of the study was to decrease the amount of added arsenic, the experiments were done without an addition of arsenic trioxide. The other cementation conditions were: $CuSO_4.5H_2O$ addition of 1.2 g/l, cementation duration of 2 hours and cementation temperature of 85°C. In all of the experiments, the initial pH of the synthetic leach solution was 4.0 ± 0.1. After cementation, the final pH values of the purified solutions were measured to be 5.0 ± 0.1. So the pH of the solution was allowed to reach its own equilibrium without making any adjustments.

As indicated in Table 4.8 and Figure 4.7, the more 10%Sn-Zn dust was added to the synthetic solution, the more precipitation of cobalt occurred. Up to an addition of 6 g/l zinc alloy dust, the cementation of cobalt increased substantially. Beyond this amount, the cobalt cementation increased slowly. For example, by adding 16 g/l of 10%Sn-Zn alloy powder, the amount of cobalt in the solution could be decreased to less than 1 ppm. Although 0.55 ppm of cobalt in purified solution with the addition of such a high amount of alloy powder is desirable, this means too much consumption of zinc alloy dust. So, to minimize the consumption of 10% tin containing zinc alloy and for the comparison of results with the results of previous experiments done using 4.0%Sn zinc alloy powder, the amount of it was chosen as 4 g/l and the additions of other reagents were optimized. If the aim is to decrease cobalt in electrolyte to about 2 ppm like at Çinkur, than 10 g/l alloy addition, which corresponds to an initial Sn/Co weight ratio of 13.25:1, will be enough.

Table 4.8. Results of Cobalt Cementation with Varying 10%Sn-Zn Alloy Addition

Exp. No	Amount of As_2O_3 Added (g/l)	Amount of 10%Sn-Zn Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (^oC)	Sn/Co Ratio By Weight	*Co Final (ppm)	%Co Cementation
42	0	2	1.2	2	85	2.65/1	52.2	30.58
43	0	3	1.2	2	85	3.98/1	30.6	59.31
44	0	4	1.2	2	85	5.31/1	22.6	69.95
45	0	6	1.2	2	85	7.95/1	7.20	90.42
46	0	8	1.2	2	85	10.6/1	9.60	87.23
47	0	10	1.2	2	85	13.25/1	2.20	97.07
48	0	12	1.2	2	85	15.9/1	3.08	95.90
49	0	14	1.2	2	85	18.55/1	0.77	98.97
50	0	16	1.2	2	85	21.2/1	0.55	99.27

*Initial cobalt concentration was 75.2 ppm

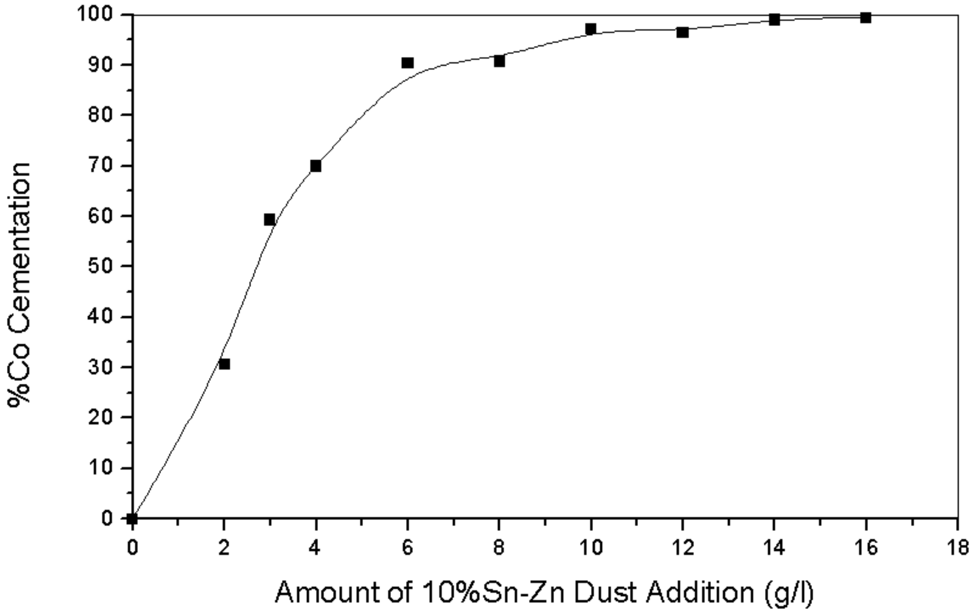

Figure 4.7. The Effect of Amount 10%Sn-Zn Alloy Dust Addition on Cobalt Cementation

4.3.2.2. Effect of the Amount of As_2O_3 Addition on Cobalt Cementation

The effect of the amount of solid arsenic trioxide added to the synthetic pregnant leach solution was investigated secondly. In these experiments, the amount of As_2O_3 added was varied between 0 and 0.22 g/l. In all of the experiments related to arsenic trioxide, the other variables were kept constant as follows: $CuSO_4.5H_2O$ added 1.2 g/l, precipitation temperature of 85°C, precipitation duration of 2 hours, and amount of zinc alloy powder 4.0 g/l.

As seen from the Table 4.9 and Figure 4.8, the percentage of Co precipitation increased from 69.95% to 89.94% with the addition of only 0.04 g/l As_2O_3. Further additions of arsenic did not change the efficiency of cobalt cementation too much. If the least amount of arsenic trioxide consumption is aimed for, 0.04 g/l of arsenic trioxide addition could be selected. However, as seen from Table 4.9, cobalt had the maximum cementation efficiency with the addition of 0.12 g/l As_2O_3. Some experiments were also conducted with 0.04 g/l arsenic trioxide with the addition of varying amounts of copper sulfate while keeping the other variables constant. Unfortunately, the cobalt cementation efficiencies were not very high. An efficiency of 86.00% was achieved with the addition of 0.4 g/l copper sulfate. With the addition of 2 g/l copper sulfate, the efficiency decreased further to 75.16%.

From the findings, it is obvious that the addition of As_2O_3 to the system had a beneficial effect on cobalt cementation. If the zinc alloy dust amount was chosen to be 6 or 8 g/l, with the addition of small amount of arsenic, the efficiency of cobalt cementation would be expected to be better.

Table 4.9. Results of Cobalt Cementation with Varying Arsenic Trioxide Addition using 10% Sn-Zn Alloy

Exp. No	Amount of As_2O_3 Added (g/l)	Amount of 10%Sn-Zn Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (°C)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
44	0.00	4	1.2	2	85	75.2	22.6	69.95
51	0.04	4	1.2	2	85	75.2	6.81	89.94
52	0.06	4	1.2	2	85	75.2	6.18	90.78
53	0.08	4	1.2	2	85	75.2	8.90	88.16
54	0.10	4	1.2	2	85	75.2	6.89	90.84
55	0.12	4	1.2	2	85	75.2	6.58	91.25
56	0.14	4	1.2	2	85	75.2	6.90	90.82
57	0.16	4	1.2	2	85	75.2	8.79	90.24
58	0.18	4	1.2	2	85	75.2	7.34	88.31
59	0.20	4	1.2	2	85	75.2	8.95	88.09
60	0.22	4	1.2	2	85	75.2	8.78	88.32

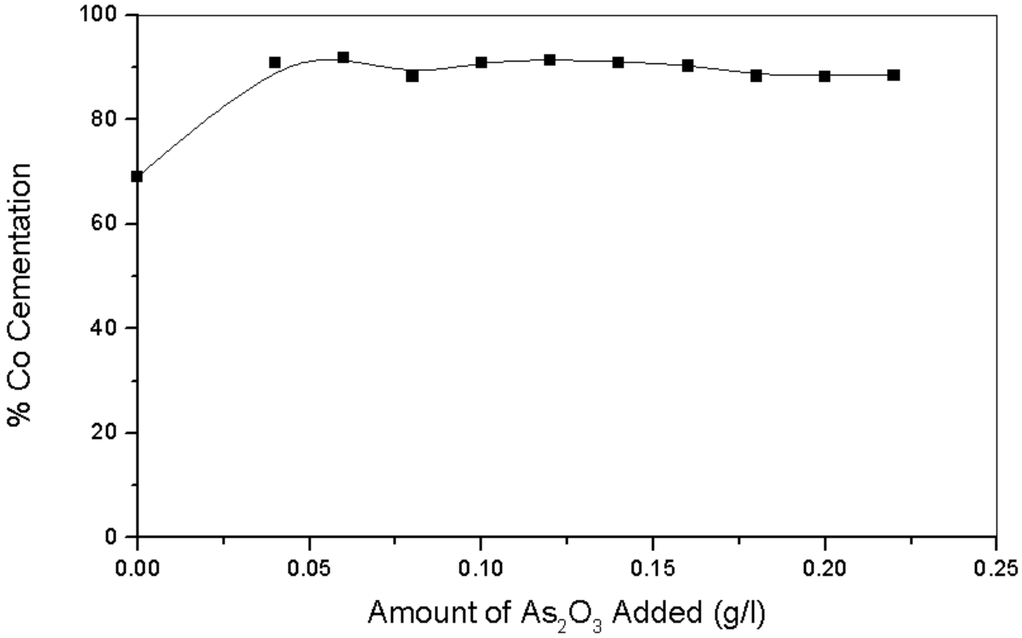

Figure 4.8. The Effect of Amount of As_2O_3 Addition on Cobalt Cementation using 10% Sn-Zn Alloy Powder

4.3.2.3. Effect of the Amount of Copper Sulfate Addition on Cobalt Cementation

The amount of the copper sulfate addition to the synthetic leach solution was investigated thirdly. The other variables were kept constant as: 0.12 g/l As_2O_3, 85°C precipitation temperature, 2 hours precipitation duration and 4.0 g/l Zn alloy powder.

Without any copper ion addition cobalt precipitation was only 38.83%. With the addition of 1.2 g/l of copper sulfate, the cobalt precipitation was increased to 91.25%. It is obvious that in order to cement out cobalt efficiently, copper ions must be added to the solution. Copper assists in the removal of cobalt. It should also be noted that there was a decrease in the amount of cobalt precipitated especially with the excessive addition of copper ions.

As a result, it can be concluded that the addition of limited amount of copper was beneficial for cobalt cementation. The optimum amount could be taken as 2 g/l since the highest cobalt cementation occurred at that initial copper sulfate concentration.

Table 4.10. Results of Cobalt Cementation with Varying Copper Sulfate Addition using 10% Sn-Zn Alloy Powder

Exp. No	Amount of As_2O_3 Added (g/l)	Amount of 10%Sn-Zn Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (°C)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
63	0.12	4	0	2	85	75.2	46.0	38.83
55	0.12	4	1.2	2	85	75.2	6.58	91.25
64	0.12	4	2	2	85	75.2	5.66	92.47
65	0.12	4	4	2	85	75.2	10.0	86.68

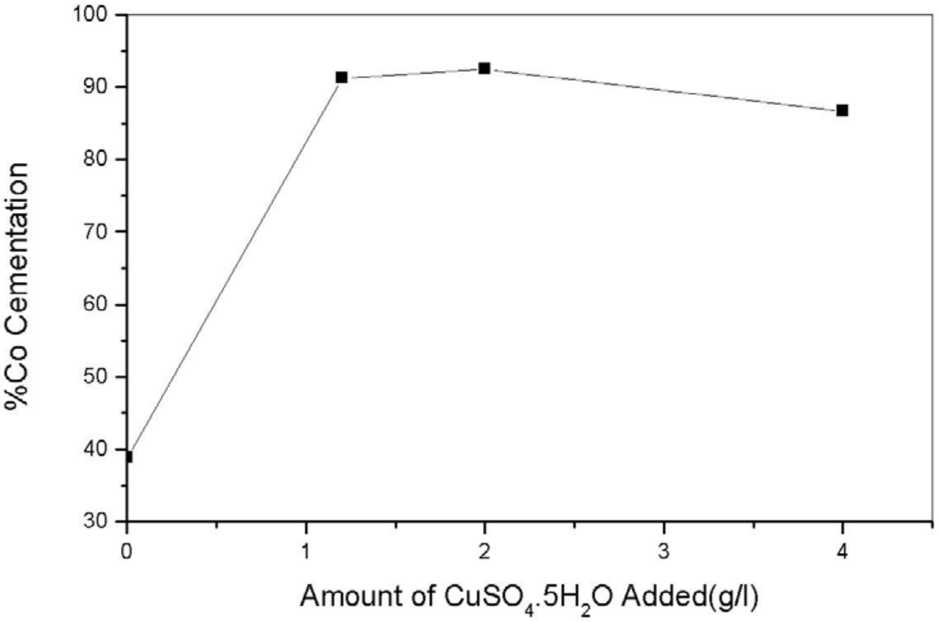

Figure 4.9. The Effect of Copper Sulfate Addition on Cobalt Cementation using 10% Sn-Zn Alloy Powder

4.3.2.4. Effect of Cementation Temperature on Cobalt Cementation

As previous observed from the experiments and stated in the literature, the removal of cobalt is poor at low temperatures. To attain a high degree of cobalt precipitation a high temperature is required. The cobalt cementation results with 1.2 g/l copper sulfate, 0.12 g/l arsenic trioxide and 4 g/l Zn alloy dust addition are given in Table 4.11 and Figure 4.10. The amount of copper sulfate was selected as 1.2 g/l for the experiments in order to compare the results with the results of 4%Sn-Zn alloy dust. Under these constant conditions and within the temperature range studied, the optimum cementation temperature was 85°C.

Temperature had a pronounced effect on the outcome of cobalt cementation. From Figure 4.10, it can be seen that there was a significant increase in precipitation of cobalt with the increase of temperature. Somewhat a similar increase in the cobalt cementation with the increasing temperature was observed with use of 4.0% Sn-Zn alloy powder.

Table 4.11. Results of Cobalt Cementation with varying Temperature using 10% Sn-Zn Alloy Powder

Exp. No	Amount of As_2O_3 Added (g/l)	Amount of 10%Sn-Zn Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Duration of Exp. (hr)	Temp. of Exp. (°C)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
66	0.12	4	1.2	2	25	75.2	68.92	8.35
67	0.12	4	1.2	2	60	75.2	34.88	53.62
56	0.12	4	1.2	2	85	75.2	6.58	91.25

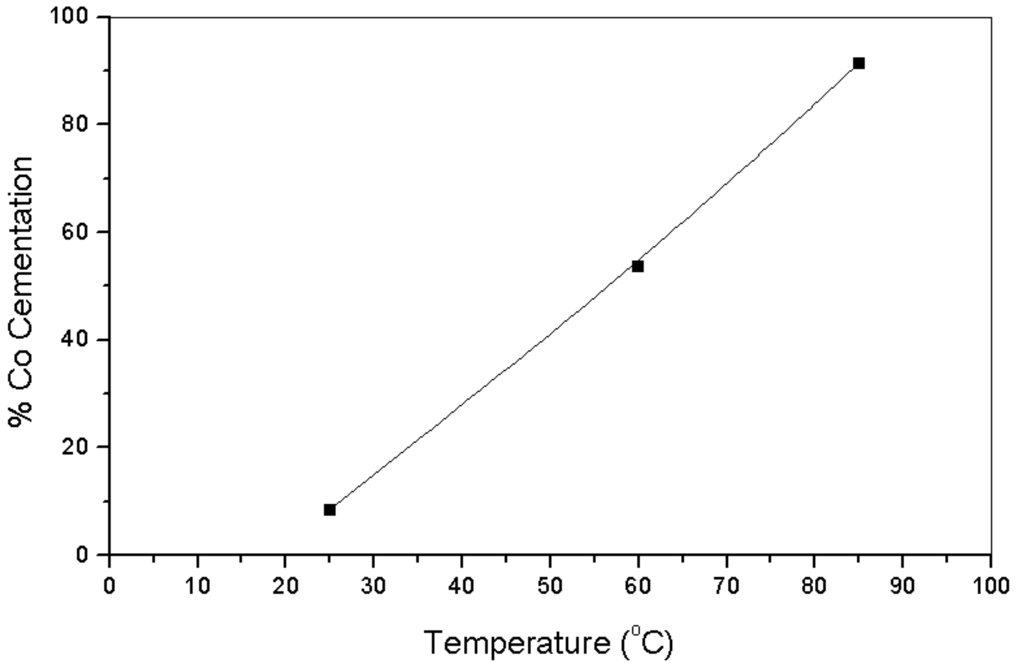

Figure 4.10. The Effect of Temperature on Cementation of Cobalt using 10% Sn-Zn Alloy Powder

4.3.2.5. Effect of Cementation Duration on Cobalt Cementation

The last parameter investigated was the effect of cementation duration on cobalt precipitation. The experiments were carried out by changing the duration between 1 hour and 5 hours. The other variables kept constant as in the investigation of the other parameters were as follows: 0.12 g/l As_2O_3, 1.2 g/l $CuSO_4.5H_2O$ and 4 g/l zinc alloy dust, 85°C cementation temperature.

It can be seen from Table 4.12 and Figure 4.11 that, there was an increase in the amount of cobalt cementation up to 2 hours. Beyond 2 hours there was a little decrease in the cobalt cementation efficiency. This little drop could be due to the reversion of the reaction due to redissolution of the cobalt containing cementate. It can be said that the shape of the curves obtained with the addition of 4.0% Sn containing zinc dust and 10% Sn containing zinc dust under the same conditions were very similar.

Table 4.12. Results of Cobalt Cementation with Duration using 10% Sn-Zn Alloy Powder

Exp. No	Amount of As_2O_3 Added (g/l)	Amount of 10%Sn-Zn Added (g/l)	Amount of $CuSO_4.5H_2O$ Added (g/l)	Duration of Exp. (hr)	Temperature of Exp. (°C)	Co Initial (ppm)	Co Final (ppm)	%Co Cementation
68	0.12	4	1.2	1	85	75.2	8.66	66.54
56	0.12	4	1.2	2	85	75.2	6.58	91.25
69	0.12	4	1.2	5	85	75.2	7.3	90.29

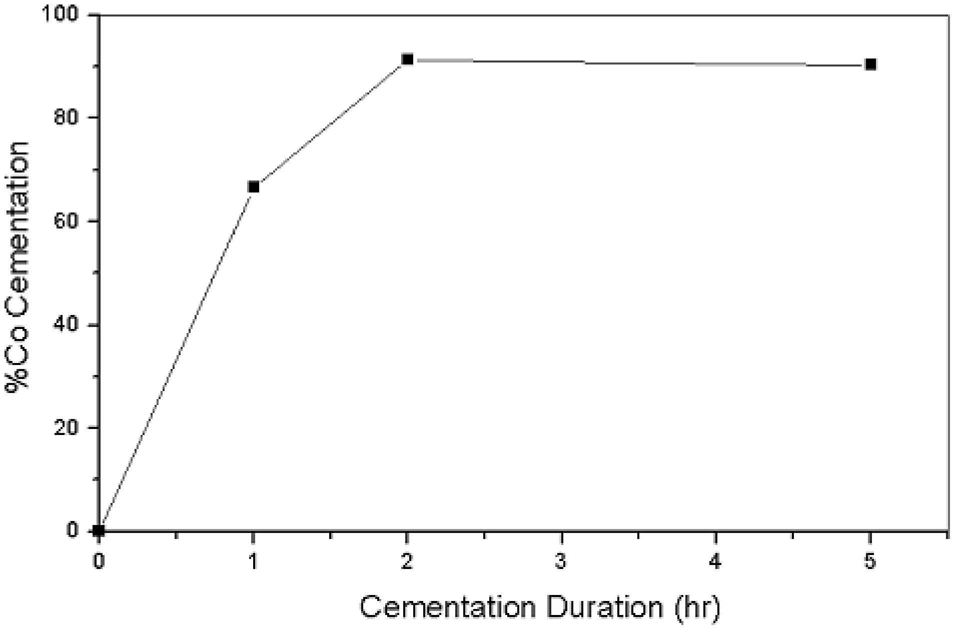

Figure 4.11. The Effect of Duration on Cobalt Cementation using 10% Sn-Zn Alloy Powder

4.4. X-Ray Diffraction and SEM Analyses of Cementates

The precipitated or cemented products, i.e., cementates, may be a mixture of metals, alloys, basic salts and sulfates. Scanning electron microscopy (SEM) and different kinds of X-ray methods can be used to characterize the porous cemented product formed on the zinc surface.

In this study, the washed cementates were ground in a mortar in order to have a homogenous powder before analysis. First, the X-ray diffraction (XRD) studies of the samples were done. Then, the samples were pressed and than gold plated for SEM analysis in order to increase the conductivity.

4.4.1. XRD and SEM Analyses Results of Zinc Powder Purification Precipitates

X-Ray diffraction diagram showed that zinc was the predominant phase in the cementation residues, as seen in Figure 4.12. Zinc existed in the form of basic zinc sulfate [$3Zn(OH)_2.ZnSO_4.5H_2O$] and hydrated zinc sulfate ($ZnSO_4.4H_2O$) and ($ZnSO_4.6H_2O$).

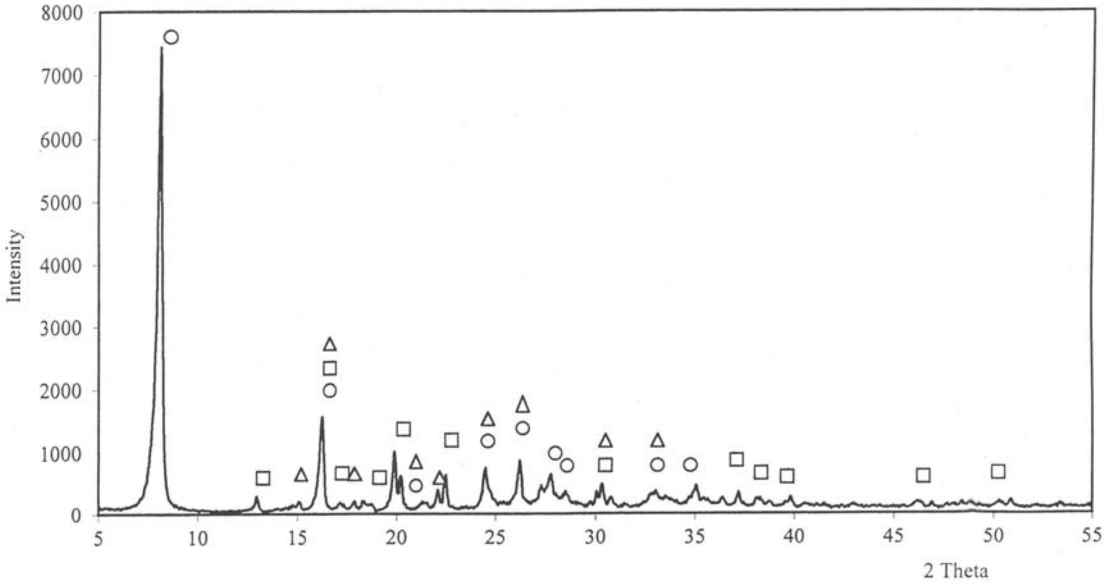

Figure 4.12. XRD Analysis of As-Cu-Co Containing Cementate

o: peaks of basic zinc sulfate, □: peaks of $ZnSO_4.4H_2O$,

Δ: peaks of $ZnSO_4.6H_2O$

SEM analysis showed an almost undetectable cobalt peak for the cementation residue containing no arsenic as seen in Figure 4.13. The cobalt peak was not visible in the particular SEM aerial analysis due to the low amount of cobalt in cementate. As seen in Figure 4.14, with the addition of arsenic and zinc but in the absence of copper sulfate the peak of cobalt became more visible. It's clear from Figure 4.15 that, with the addition of all the additives, the peaks of Co, As and Cu were apparent. SEM analysis showed that zinc, sulfur, arsenic, copper and cobalt all existed in the cementates. From this analysis, it can be concluded that either a mixed Co, Cu, As compound occurred on basic zinc sulfate or CoAs or $CoAs_2$ phase occurred on copper arsenide substrate.

More detailed results could not be obtained with the available SEM in the Department. For better analysis of the cementates, a microprobe study was necessary since the intermetallic phases were very small in size.

4.4.2. XRD and SEM Analyses Results of Zinc Alloy Powder Purification Precipitates

X-Ray diffraction diagrams of cementates for both of the tin containing zinc alloys showed similar patterns to that of pure zinc powder. As stated before in the X-Ray analysis of the cementate with pure zinc dust addition, basic zinc sulfate and hydrated zinc sulfates were the predominant phases.

In SEM analysis of cementates obtained without any arsenic addition, the peaks of Cu, Co and Sn could be detectable as seen in Figure 4.16. This indicated the possibility of the presence of CuSn, CoSn and CoCuSn on basic zinc sulfate. Figure 4.17 showed the peaks of cemented elements when no copper sulfate was added into the solution. When arsenic trioxide was added into the solution, it took part in the cementation and appeared in the SEM analysis of the cementate as seen in Figure 4.18. The cementated compound was not obvious but might be a mixed Co, Cu, As, Sn compound.

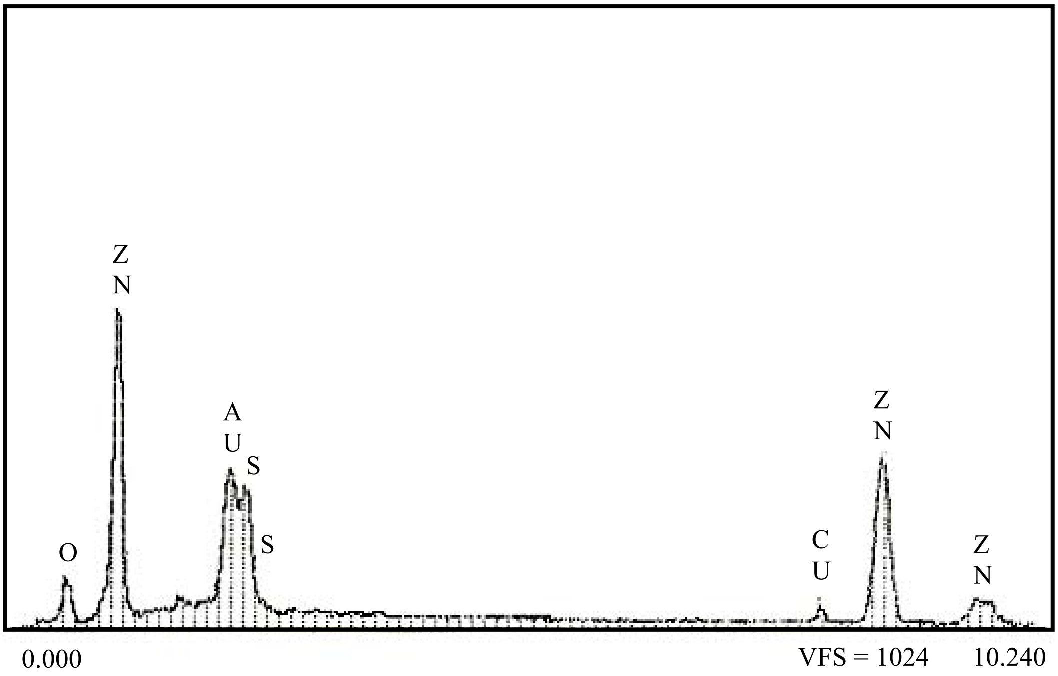

Figure 4.13. SEM Diagram of Cementate Obtained with the Use of Pure Zinc Powder and without the Addition of Arsenic Trioxide

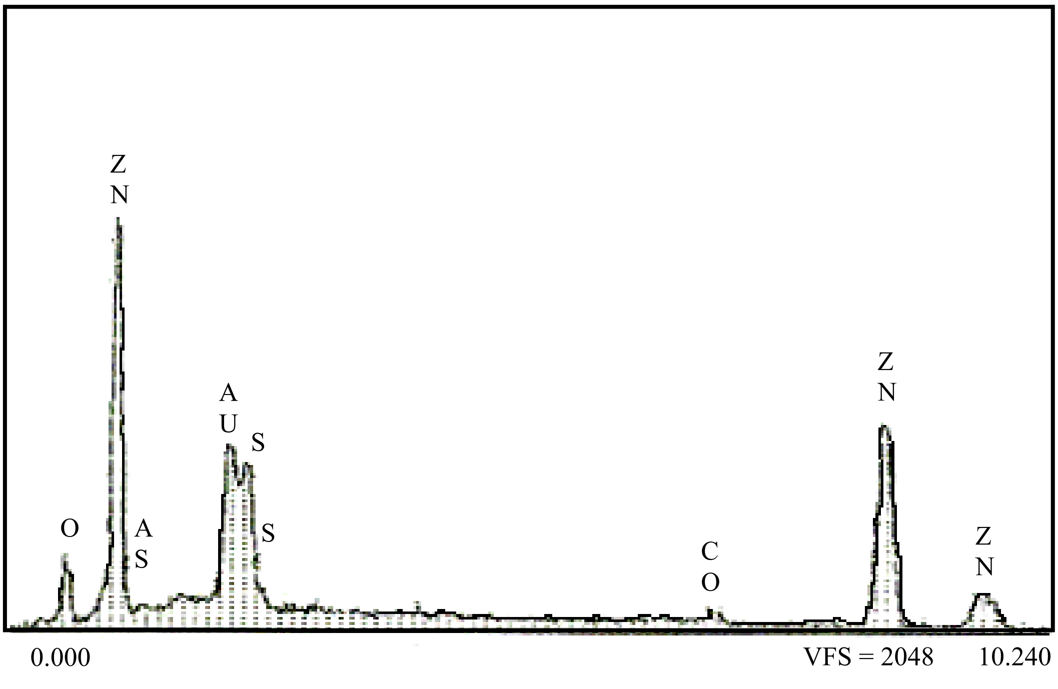

Figure 4.14. SEM Diagram of Cementate Obtained with the Use of Pure Zinc Powder and without the Addition of Copper Sulfate

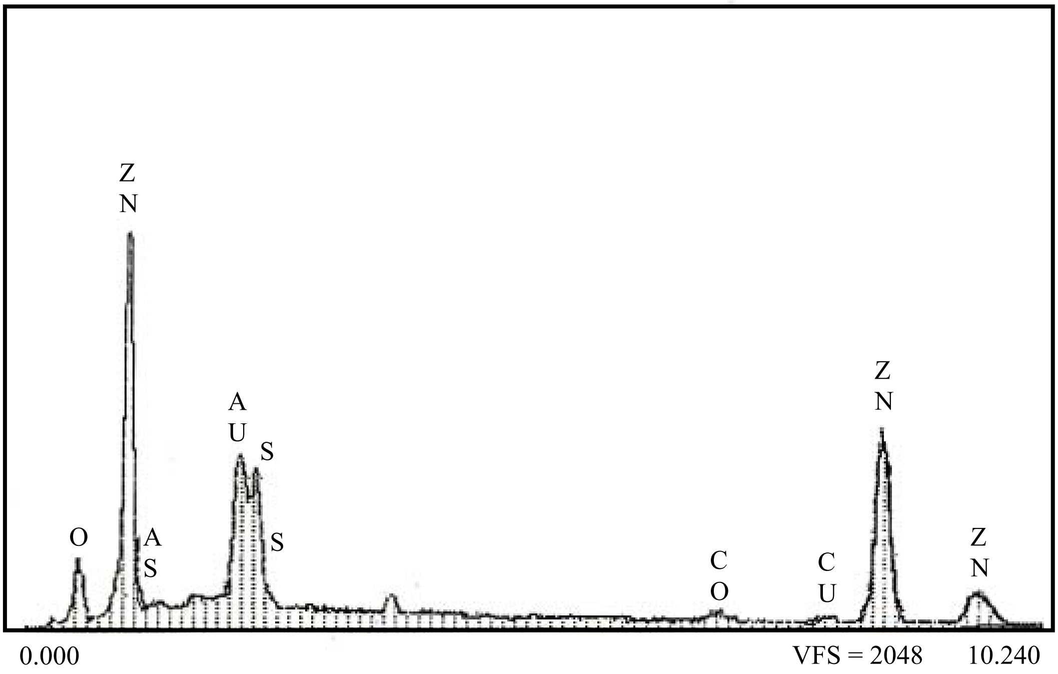

Figure 4.15. SEM Diagram of Cementate Obtained with the Use of Pure Zinc Powder, with the Addition of Arsenic Trioxide and Copper Sulfate

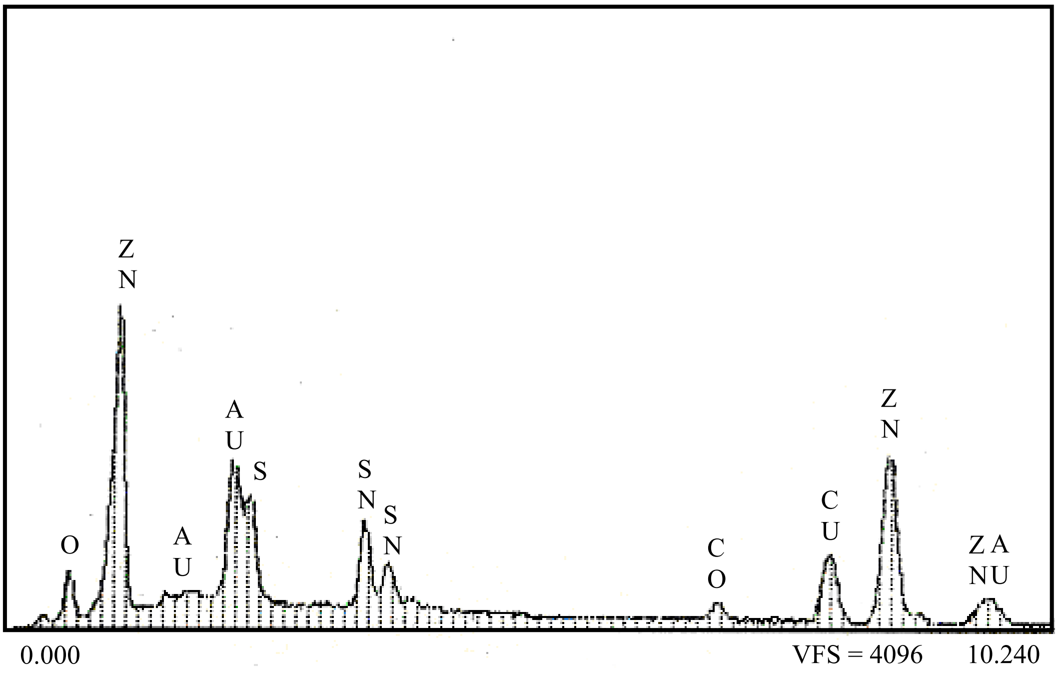

Figure 4.16. SEM Diagram of Cementate Obtained with the Use of Alloy Zinc Powder, without the Addition of Arsenic Trioxide

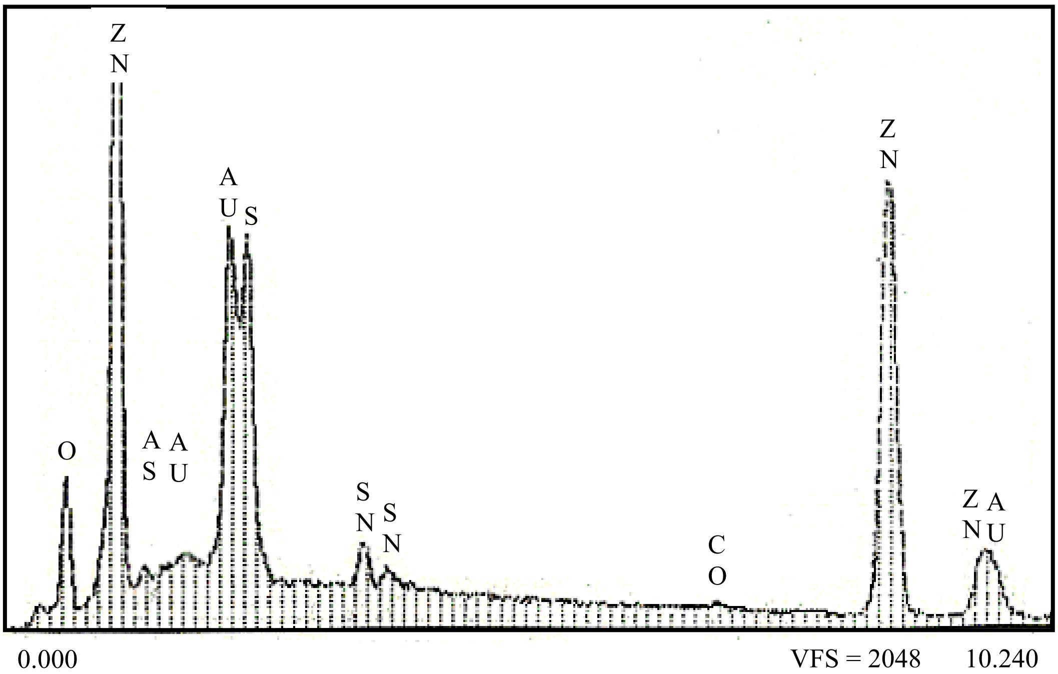

Figure 4.17. SEM Diagram of Cementate Obtained with the Use of Alloy Zinc Powder, without the Addition of Copper Sulfate

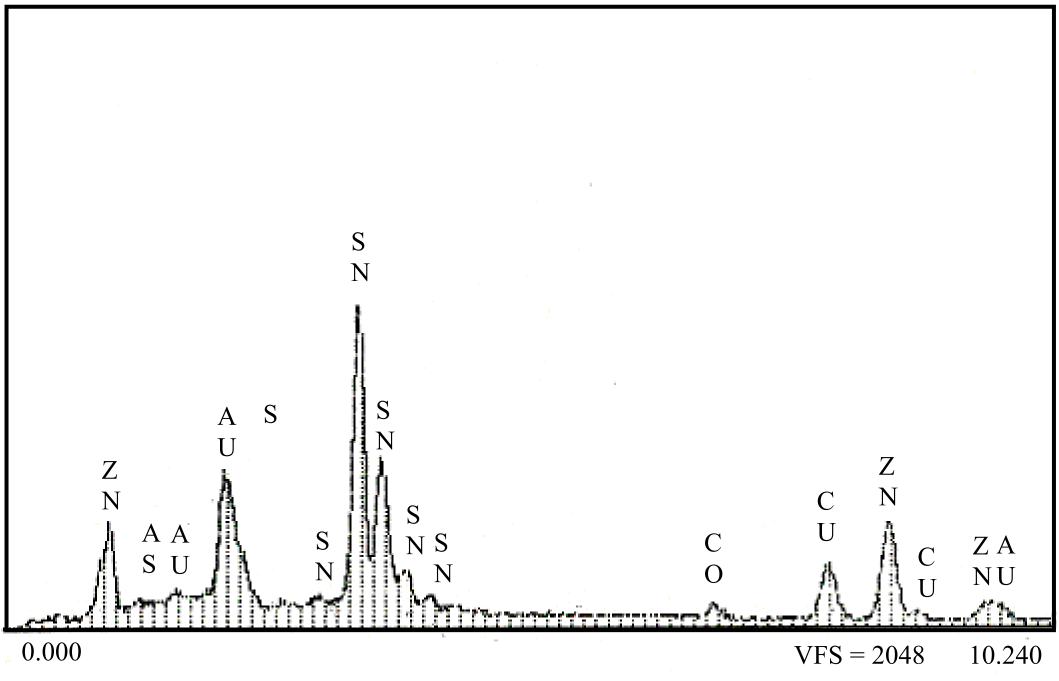

Figure 4.18. SEM Diagram of Cementate Obtained with the Use of Alloy Zinc Powder, Arsenic Trioxide and Copper Sulfate

4.5. Comparison of the Cobalt Cementation Results

In this section, the results of cementation of cobalt obtained with pure zinc powder are compared with those obtained by the use of the alloy powders. On the other hand, the comparison of the results of two different types of alloy is also done.

4.5.1. Comparison of Pure Zinc and 4% Tin-Zinc Alloy Powders

The cementation of cobalt with 4%Sn-Zn alloy dust gave much better results than the cementation with pure zinc dust. The efficiency of cementation of cobalt was always higher with the same amount of arsenic addition as seen in Figure 4.19. In this comparison constant parameters were: 4 g/l pure zinc or alloy addition, 0.4 g/l copper sulfate addition, 2 hours cementation duration and 85°C cementation temperature. Also, the excessive amounts of arsenic trioxide addition were detrimental to the precipitation of cobalt in both series of experiments. The maximum cementation of cobalt was 91.37% with 0.12 g/l As_2O_3 addition using the alloy.

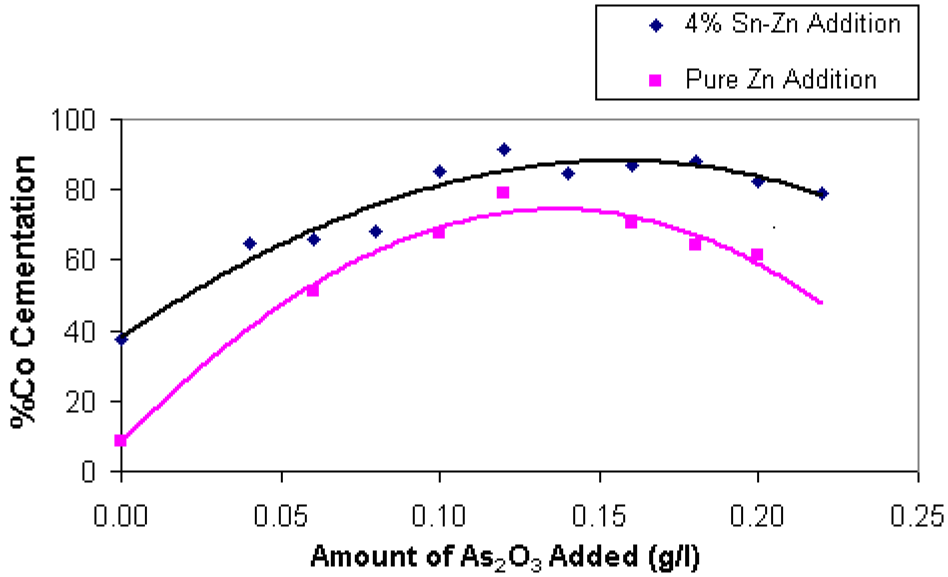

Figure 4.19. Comparison of the Effect of Amount of As_2O_3 Added on Cobalt Cementation using Pure Zinc Powder and 4% Sn-Zinc Alloy Powder

4.5.2. Comparison of the Two Alloys

The two alloys were compared with respect to cobalt cementation with varying copper sulfate addition, cementation duration and cementation temperature.

4.5.2.1. Comparison of the Two Alloys with Varying Copper Sulfate Addition

The comparison of the two zinc alloys, one containing 4%Sn and the other one containing 10% Sn with respect to cobalt cementation with varying copper sulfate addition is given in Figure 4.20. In this comparison constant parameters were: 4 g/l zinc alloy addition, 0.12 g/l As_2O_3 addition, 2 hours cementation duration and 85°C cementation temperature. As it can be seen for the figure, except with no addition of copper sulfate, the alloy with 4% Sn always gave better results. The copper ion addition in the form of copper sulfate was essential in both cases in order to obtain meaningful cobalt cementation results. The excessive additions of copper were detrimental in cobalt cementation with the use of either alloy. The maximum cobalt cementation of 96.73% was reached with an addition of 1.2 g/l copper sulfate which corresponded to about 2 ppm in the purified synthetic solution.

4.5.2.2. Comparison of the Two Alloys with Varying Cementation Duration

The cobalt cementation with both alloys was affected in a similar manner with varying cementation duration as seen in Figure 4.21. In this comparison constant parameters were: 4 g/l zinc alloy addition, 0.12 g/l As_2O_3 addition, 1.2 g/l $CuSO_4.5H_2O$ addition, 85°C cementation temperature. The zinc alloy with 4% tin gave slightly better results. In both cases, the maximum cobalt cementation was obtained in 2 hours.

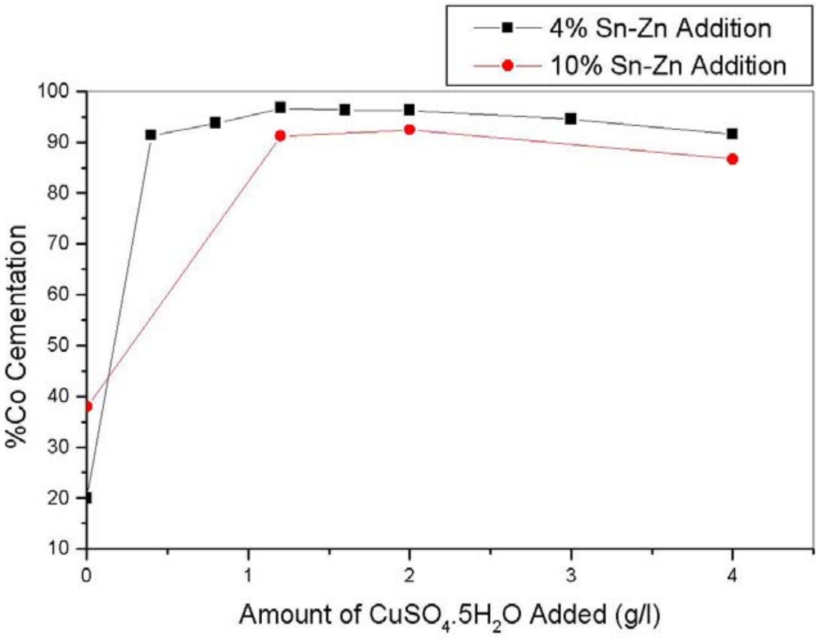

Figure 4.20. Comparison of the Effect of Amount of Copper Sulfate Added on Cobalt Cementation using 4% Sn-Zinc and 10% Sn-Zinc Alloy Powder

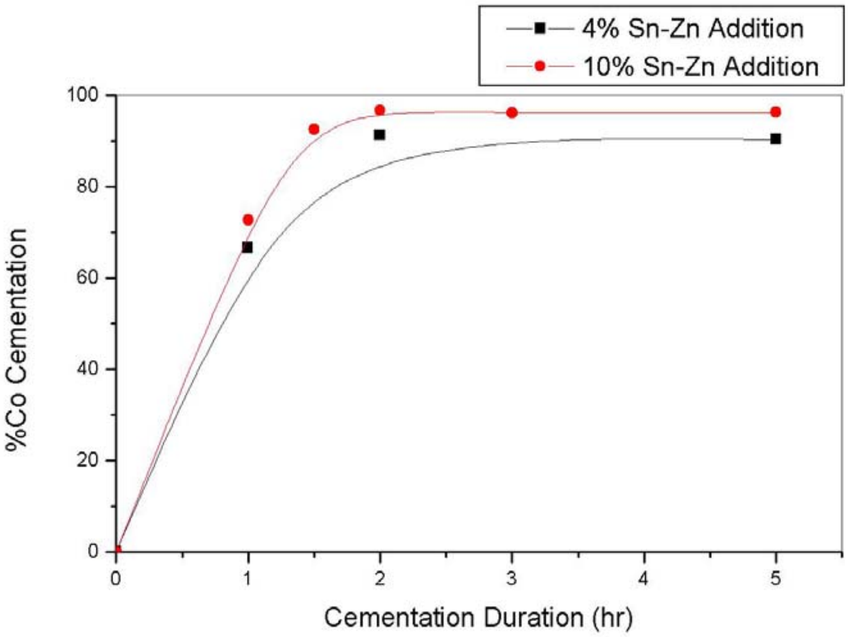

Figure 4.21. Comparison of the Two Alloys with Varying Cementation Duration

4.5.2.3. Comparison of the Two Alloys with Varying Cementation Temperature

Finally, the two alloys were compared with respect to cobalt precipitation temperature. In this comparison constant parameters were: 4 g/l zinc alloy addition, 0.12 g/l As_2O_3 addition, 1.2 g/l $CuSO_4.5H_2O$ addition, 2 hours cementation duration. As seen from Figure 4.22 that, whether 4% or 10% Sn-Zinc alloy powder is used for the cementation of cobalt, similar results were obtained. The highest cobalt cementations were obtained at the temperature range of 85 to 90°C. Again, 4% tin containing alloy gave slightly better precipitation results.

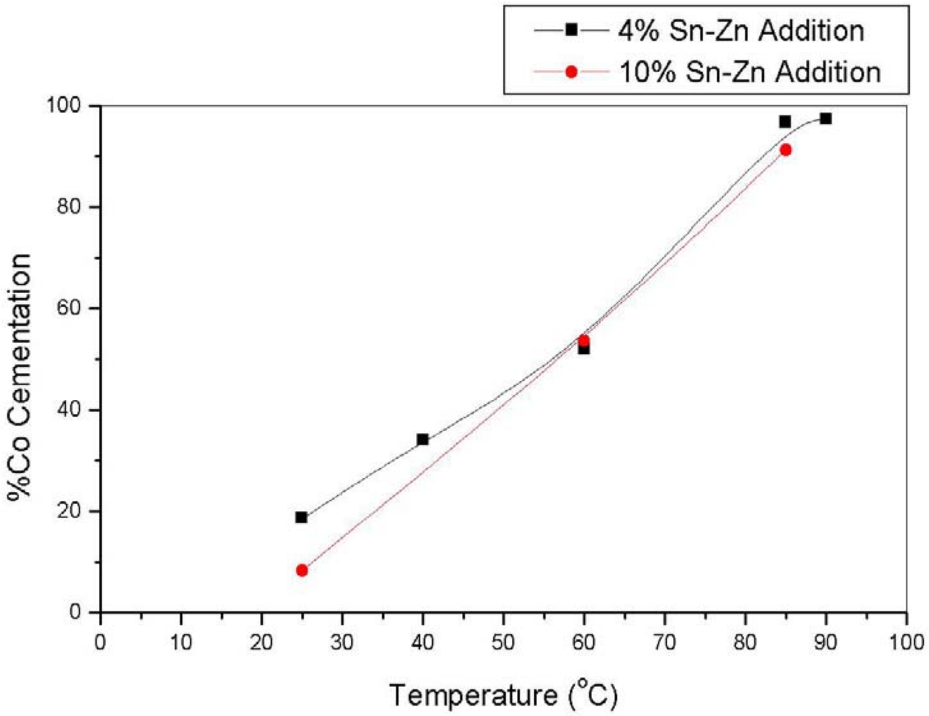

Figure 4.22. Comparison of the Two Alloys with Varying Cementation Temperature

CHAPTER 5

CONCLUSIONS

The aim of this study was to investigate the removal of cobalt from zinc sulfate solution by cementation with the help of conventional and new type of additives. For this purpose, synthetic leach solutions containing 150 g/l Zn and 75 mg/l Co were prepared and used in all of the experiments.

The first set of experiment was conducted with pure zinc powder as in Çinkur and the obtained results were used for comparison purposes. In the second and third series of tests, the cobalt cementation with 4% Sn-zinc alloy powder and 10% Sn-zinc alloy powder were studied, respectively.

The obtained results indicated that tin containing alloys were much better than pure zinc powder in the precipitation of cobalt from the synthetic solution. In fact, it was shown that without the use of arsenic trioxide, the precipitation of cobalt was possible with the alloys although excessive uses of the alloys were necessary. Cobalt levels of less than 1 ppm were achieved with use of more than 14 g/l alloy containing 10% tin.

As the tin content increased from 4% to 10% in the new type of alloy powder, there was a decrease in the amount of cobalt precipitated from the solution. Most of the experiments involving 4% Sn-zinc alloy powder gave better results. As the duration and temperature of cementation increased there was an increase in the amount of cobalt precipitated. The optimum duration of cementation was found to be 2 hours and the optimum temperature range of cobalt precipitation was 85°C to 90°C. The experiments indicated that cobalt in the solution could be reduced to about 2 ppm by using an initial Sn/Co weight ratio of 13.25:1 without the addition of arsenic trioxide. Although, this was a high ratio when compared to the values given in the literature, in the industry the cobalt concentrations of the solutions usually change in the range of 5-30 ppm. The synthetic solutions used in the experiments in this study contained 75 ppm cobalt. If the Sn/Co ratio was decided to be 2.12:1 as in the literature, then a small amount of arsenic trioxide addition was needed to have high cementation efficiency. Excessive additions of arsenic trioxide were found to be undesirable in cobalt cementation.

In spite of this high cobalt content of the synthetic solution, the consumption of arsenic was within the range of the amount of arsenic used in the zinc industry, which is 0.07 to 0.2 g/l of impure electrolyte. In the experiments, the optimum amount of arsenic trioxide consumption was 0.12 g/l.

The zinc dust consumption in the zinc industry is 25 to 45 kg per ton of electrolytic zinc. The consumption of zinc dust in this study was 26.6 kg per ton of electrolytic zinc which was an acceptable amount.

The consumption of copper ions added as 1.2 g/l copper sulfate was a little bit high when compared to the amount used at Çinkur (0.4 g/l copper sulfate), but it was clearly seen that without the addition of limited amount of copper sulfate to the solution, the cementation of cobalt was not successful. Excessive additions of copper sulfate were found to be detrimental in cobalt cementation. Impure zinc electrolyte typically contains 0.5 to 1.0 g/l copper (equals to 1.96 to 3.92 g/l copper sulfate) in the zinc industry. Due the presence of copper minerals in most zinc ores, the amount of copper in impure electrolyte varies. So, the extra addition of copper sulfate depends on the amount of copper ions already present in the impure electrolyte.

The XRD analysis of the cementates indicated that the cementates were mainly composed of hydrated zinc sulfate and basic zinc sulfate. The SEM analysis of the cementates of pure zinc indicated that either a mixed Co, Cu, As compound occurred on basic zinc sulfate or CoAs or $CoAs_2$ phase occurred on copper arsenide substrate. In SEM analysis of cementates obtained with alloy additions without the use of arsenic, the peaks of Cu, Co and Sn could be detectable. This indicated the possibility of the presence of CuSn, CoSn and CoCuSn on basic zinc sulfate. When arsenic trioxide was added into the solution, it took part in the cementation and appeared in the SEM analysis. The precipitated compound was not obvious but might be a mixed Co, Cu, As, Sn compound.

In conclusion, it can be said that since when used as an activator for cobalt precipitation, As_2O_3 gives highly toxic gases, which causes severe environmental problems, and detrimental to the health of operating workers, a new additive can replace it. This new additive can be a zinc alloy powder containing tin as indicated in this thesis. Without any arsenic trioxide addition, it is possible to precipitate cobalt. But to obtain high cobalt cementation efficiencies, excessive amount of alloy has to be consumed. The other disadvantage of the alloy will be its higher cost.

Future work recommended:

1. Experiments with the new additive should be continued with different Zn-Sn alloy compositions.
2. Experiments can be done under argon atmosphere instead of air to prevent oxidation reactions.
3. The use of cementate obtained from the first precipitation step in the following precipitation steps (i.e., recycling) should be undertaken. So seeding of the solution should accelerate cobalt precipitation.

4. Experiments can be conducted with solutions at different initial pH values.
5. Experiments should be conducted to recover cobalt and other valuable metals from the cementates.
6. Precipitation of cobalt can be done with multistage operations rather than a single-stage operation. Addition of reagents in a stepwise manner should also be studied.
7. Solutions containing different amounts of cobalt should be used in the experiments in order to investigate the effect of initial cobalt concentration.
8. The experiments should be repeated with real pregnant leach solutions containing other impurities besides cobalt.
9. Arsenic trioxide should be dissolved in NaOH instead of adding in the solid form. However, in these experiments the pH of the solution should be controlled below 5.4 by acid addition in order to prevent basic zinc sulfate precipitation on zinc powder.
10. The effect of pure zinc or alloy particle size should be investigated. For this purpose the powders that will be used in the experiments, should be closely sized by screening.
11. The effect of stirring speed on cementation should be studied.
12. New additives should be identified that can lead to a more efficient purification process and these new additives should be tested with synthetic and real electrolyte solutions.
13. Arsenic, copper, tin, etc, analysis of the solution should be also followed during the precipitation reaction so as to detect the variations for better interpretation of the experimental results.
14. Cementates should be investigated under a microprobe for the identification of intermetallics of very small size.

REFERENCES

1. Lew R.W., Dreisinger D.B., Gongalez-Dominguez J.A., The Removal of Cobalt from Zinc Sulfate Electrolytes Using Copper-Antimony Process: Kinetics, Mechanisms and Morphological Characterisation, World Zinc International Symposium, Tasmania, The Australian Institute of Mining and Metallurgy, pp.227-240, October, 1993

2. Mathewson C.H., Zinc: The Science and Technology of the Metal, Its Alloys and Compounds, Hafner Publishing Company Inc., 1970

3. Nelson A., Wang W., Demopoulos G.P., Houlachi G., The Removal Of Cobalt from Zinc Electrolyte by Cementation: A Critical Review, Mineral Processing and Extractive Metallurgy Review, Vol.20, pp. 325-356, 2000

4. Minerals.usgs.gov/minerals/pubs/commodity/zinc

5. U.S Patent 4,240,826, December 23, 1980

6. Tozawa K., Proceedings of International Symposium on Extractive Metallurgy of Zinc, Japan, 1985

7. http://www.ilzsg.com

8. Cobalt News, Published by the Cobalt Development Institute, January, 2000

9. Shedd K., Annual Review of Cobalt, U.S. Department of the Interior, U.S. Geological Survey, Mineral Industry Surveys, 1998

10. International Conference on Cobalt: Metallurgy and Uses, Proceedings Vol.1, Brussels, Belgium, November 1981, organized by Benelux Metallurgie with the logistic aid of the Centre

11. Cobalt News, Published by the Cobalt Development Institute, October 2001

12. http://mineral.galleries.com/minerals

13. Nelson A., Demopoulos G.P., Houlachi G., The Effect of Solution Constituents and Novel Activators on Cobalt Cementation, Canadian Metallurgical Quarterly, Volume 39, No.2, pp. 175-186, 2000

14. Lawson F., Nhan L.T., Kinetics of Removal of Cobalt from Zinc Sulfate Electrolytes by Cementation, Hydrometallurgy'81, Proceedings of Society of Chemical Industry Symposium, Manchester, June, 1981

15. Fountoulakis S.G., Studies on the Cementation of Cobalt with Zinc in the Presence of Copper and Antimony Additives, Ph.D. Thesis, Columbia University, 1983

16. Dreher T.M., Nelson A., Demopoulos G.P., Filippou D., The Kinetics of Cobalt Removal by Cementation from an Industrial Zinc Electrolyte in the Presence of Cu, Cd, Pb, Sb and Sn Additives, Hydrometallurgy, 60, pp. 105-116, 2001

17. Ault A.R., Frazer E.J., Smith G.D.J., Journal of Applied Electrochemistry, 18, 1988

18. Sandberg G., Hebble T.L., Cobalt and Nickel Removal from Zinc Sulfate Electrolyte by Solvent Extraction and Precipitation Techniques, USBM, RI 8320, 1978

19. Singh V., Technological Innovation in the Zinc Electrolyte Purification Process of a Hydrometallurgical Zinc Plant Through Reduction in Zinc Dust Consumption, Hydrometallurgy, 40, pp.247-262, 1996

20. Van der Pas V., Dreisinger D.B., A Fundamental Study of Cobalt Cementation by Zinc Dust in the Presence of Copper and Antimony Additives, Hydrometallurgy, 43, pp. 187-205, 1996

21. Deblander F., Winand R., Influence de l' Antimonie et du Cuivre sur la Cementation du Cobalt par le Zinc, Electrochim., Acta 20, pp.839-852, 1975.

22. Fontana A., Winand R., Metallurgie 11, pp.162-167, 1971

23. Kroleva V., Copper Antimonide as an Activator for Cobalt Cementation with Zinc Dust, Metalurgiya, Sofia, 1980

24. MacKinnon D.J., Brannen J.M., Kerby R.C., Journal of Applied Electrochemistry, 55, 1979

25. Nelson A., Demopoulos G.P., Houlachi G., Rosato L., Cobalt Removal from Zinc Electrolyte by Cementation: Fundamentals and New Additives, EPD Congress Proceedings, The Minerals, Metals&Materials Society, pp. 785-795, 1998

26. Blaser B.M., O'Keefe T.J., Screening Design Test for Cobalt Cementation from Zinc Electrolyte, Metallurgical Transactions B, Volume 14 B, pp.495-497, 1983

27. Borve K., Ostvold T., Norzink Removal of Cobalt from Zinc Sulfate Electrolytes, Hydrometallurgy 94, Cambridge, Chapman and Hall, London, pp.563-577, 1994

28. Esna-Ashari M., Fischer H., Purification of Solutions for the Tankhouse, Erzmetall, Vol. 36, pp.83-87, 1983, Germany

29. Raghavan R., Mohanan P.K., Verma S.K., Modified Zinc Sulfate Solution Purification Technique to Obtain Low Levels of Cobalt for the Zinc Electrowinning Process, Hydrometallurgy, 51, pp. 187-206, 1999

30. Yamashita S., Okubo M., Goto S., Hata K., Mechanism of Removal of Cobalt from Zinc Sulfate Solution for Electrowinning, Today's Technology for the Mining and Metallurgical Industries, Mining and Metallurgical Institute of Japan and the Institute of Mining and Metallurgy London, pp.83-90, 1989

31. Tozawa K., Nishimura T., Akahori M., Malaga M.A., Comparison Between Purification Processes for Zinc Leach Solutions with Arsenic and Antimony Trioxides, Hydrometallurgy, 30, pp. 445-461, 1992

32. Fugleberg S., Rantanen R., Sipila V., Jarvinen A., Solution Purification Process at the Outokumpu Kokkola Zinc Plant, 113th AIME Annual Meeting, Los Angeles, USA, 1984

33. Fugleberg S., Jarvinen A., Yllö E., Recent Development in Solution Purification at Outokumpu Zinc Plant, Kokkola, International Symposium World Zinc, pp.241-247, 1993

34. MacKinnon D.J., Kinetics of Cobalt Cementation on Zinc, Canadian Mines Branch Res., Res. Rep. 259, 20, 1973

35. Salin A.A., Tsvetn Metal, 37, pp. 53-59, 1964

36. West-Sells P.G., Dr. Thesis, University of British Columbia, 1996

37. Bockman O., Ostvold T., Products Formed during Cobalt Cementation on Zinc in Zinc Sulfate Electrolytes, Hydrometallurgy, 54, pp. 65-78, 2000

38. Cole P.M., The Introduction of Solvent-Extraction Steps During Upgrading of a Cobalt Refinery, Hydrometallurgy, 64, pp.69-77, 2002

39. Karavasteva M., The Effect of Certain Surfactants on the Cementation of Cobalt From Zinc Sulfate Solutions by Suspended Zinc Particles in the Presence of Copper and Antimony, Canadian Metallurgical Quarterly, 40, pp. 179-184, 2001

40. Wang Y., Zhou C., Hydrometallurgical Process for Recovery of Cobalt from Zinc Plant Residue, Hydrometallurgy, 63, pp. 225-234, 2002

41. Lu J., Dreisinger D.B., Cooper W.C., Cobalt Precipitation by Reduction with Sodium Borohydride, Hydrometallurgy, 45, pp. 305-322, 1997

42. Schlesinger H.J., Brown H.C., New Developments in the Chemistry of Diborane and the Borohydrides General Summary, J. Am. Chem. Soc., 75, pp. 186-190, 1953

43. Polyakov M.L., Polyakova E.M., Polyakova O.M., Removal of Metals from Zinc Sulfate Solution by Reduction with Sodium Borohydride in the Presence of Triethanolamine, USSR Patent 1,212,951, 1986

44. Awadalla F.T., Yin Z., Pesic B., Reduction of Co, Cu and Fe from Aqueous Solutions with Sodium Borohydride, TSM Annual Meeting, pp. 273-286, USA, 1989

45. DeBecker B., Peeters F., Duby P., Recovery of Chromium from Chromate Waste by Electrowinning from Cr(III) Solutions, The Minerals, Metals and Materials Society, pp.55-72, 1993

46. Yang C., Duby P., Cobalt Cementation with Ferromanganese, Hydrometallurgy, 61, pp.95-205, 2001

47. Owusu G., Oxidation-Precipitation of Co from Zn-Cd-Co-Ni Sulphate Solution Using Caro's Acid, Hydrometallurgy, 48, pp. 91-99, 1998

48. Qing-heng Z., Shi-zhen C., A New Zinc Powder for Cobalt Elimination in Depth Purification of $ZnSO_4$ Solutions, Zinc '85, pp. 127-140, 1985

49. Alper A.M., Phase Diagrams, Materials Science and Technology, Volume 1, pp.26, 1970

50. Tonder G.J., Cilliers P.J., Meyer E.H.O et. al., Cobalt and Nickel Removal from Zincor Impure Electrolyte by Molecular Recognition Technology (MRT)- Pilot Plant Demonstration, The Journal of The South African Institue of Mining and Metallurgy, pp.11-17, January/February 2002

51. Wever G.T., Effect and Control of Impurities in the Electrowinning of Zinc, JOM, 130, February 1959

52. Brewis T., Iran: Land of Opportunity, Mining Magazine, pp. 74, August 1992

53. Addemir O., Açma E., Arslan C., Çinko, Sistem Yayıncılık, 1995