ARMANDO VALENZUELA

ARSENIC MANAGEMENT IN THE METALLURGICAL INDUSTRY

Mémoire
présenté
à la Faculté des études supérieures
de l'Université Laval
pour l'obtention
du grade de maître ès sciences (M.Sc.)

Département de mines et métallurgie
FACULTÉ DE SCIENCES ET GÉNIE
UNIVERSITÉ LAVAL

SEPTEMBRE 2000

National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

0-612-55887-8

Canadä

ABSTRACT

Arsenic is one the most obnoxious impurities in the metallurgical industry, principally in copper smelters. In the last few decades, environmental regulation of arsenic has been promulgated, which has forced the smelters to treat their gases through to sulfuric acid plants in order to respect the national and international environmental standards.

The objective of this thesis is carry out a review of the effects of arsenic on human health, the solution chemistry of arsenic, the world production and uses of arsenic and its compounds in recent years. The environmental situation of the Chilean metallurgical industry, regarding the regulations and present solutions for management of SO_2, particulate matter and arsenic is particularly emphasized since Chile is the world's largest copper producer. The hydrometallurgical and the pyrometallurgical processes for arsenic recovery from gold, cobalt and copper concentrates as well as from copper smelter dusts, whether implemented or in research, are reviewed. In addition, this study considers the disposal of the arsenic emitted by metallurgical plants by precipitation under a variety of forms, for example, as ferric arsenate, calcium arsenate or arsenic sulfide.

Armando Valenzuela

Kostas Fytas

RÉSUMÉ

L'arsenic est l'une des impuretés les plus nocives dans l'industrie métallurgique et surtout dans les fonderies de cuivre. Durant les dernières années, la réglementation environnementale sur l'arsenic a obligé les compagnies métallurgiques à traiter leurs gaz dans des usines d'acide sulfurique et ce afin de pouvoir respecter les normes nationales et internationales en matière d'environnement.

Ce mémoire a pour but de présenter les effets nocifs de l'arsenic chez les êtres humains, la chimie des solutions d'arsenic ainsi qu'une analyse du marché mondial des composés d'arsenic et leurs utilisations récentes. Une analyse de la situation environnementale et de la gestion du SO_2, de la poussière et de l'arsenic dans l'industrie métallurgique chilienne est incluse, car le Chili constitue le principal producteur de cuivre au monde. Une étude précise les alternatives disponibles pour la récupération des composés d'arsenic à partir des concentrés d'or, de cobalt, et de cuivre ou à partir de la poussière des fonderies de cuivre. Finalement, cette thèse étudie la fixation de l'arsenic par précipitation sous forme d'arséniate ferrique, d'arséniate de calcium ou de sulfure d'arsenic.

Armando Valenzuela

Kostas Fytas

ACKNOWLEDGEMENTS

I would like to express my appreciation to my thesis supervisor Dr. Kostas Fytas who allowed me to realize this investigation freely.

I would like also to acknowledge the helpful comments, discussions and corrections made by my co-supervisor Dr. Fathi Habashi at the Department of Mining and Metallurgy, Laval University.

The Government of Chile has generously supported my staying at Laval University through the program "Beca Presidente de la República para Estudios de Postgrado en el Extranjero".

Special thanks are also due to the following persons who sent me information on arsenic treatment: G. Achurra, R. Araya and D. Vega from Codelco-Chile; R.M. Berezowsky from Dynatec; G.J. Coakley and J.C. Wu from the US Geological Survey; M. Sánchez from University of Concepción; M. Sández from Mexicana de Cobre; T. Terayama from Sumitomo Metal Mining; P. Valenzuela from Conama Chile and P. Rojas from Hernán Videla Lira smelter, ENAMI.

Finally, I would like to dedicate this work to my parents and my family for their continuous support and encouragement.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

The last few decades have been a serious environmental challenge for the metallurgical industry, especially for copper smelters, due to pressures from public opinion and the numerous environmental regulations imposed. Regulation of sulfur dioxide emissions has forced smelters to treat their gases directed to sulfuric acid plants to remove dust particles and any volatilized arsenic. During the smelting-converting process some arsenic also reports in the blister copper. It must be removed from the refined product otherwise it will deleteriously influence its properties. Because of its toxicity, arsenic has received great attention in the metallurgical industry.

The presence of high arsenic concentrations in the copper and gold-copper concentrates is one of the major environmental problems for the Chilean mining industry. New environmental regulations limit the arsenic emitted into the atmosphere from each smelter (CONAMA, 1999). As a consequence there will be a significant increase in the amount of arsenic residues, which will have to be managed in a safe way, whether for its recovery or disposal.

Arsenic is recovered as a by-product of processing certain complex ores that are mined mainly for copper, lead, zinc, cobalt, gold and silver, and its supply is dependent on the demand for these metals. In the past years, the market for arsenic compounds such as arsenic trioxide and arsenic metal has not grown, thus creating a surplus of arsenic production.

The disposal of arsenic has been accomplished in practice by the formation of metal arsenates and metal arsenites, e.g., of Ca^{2+}, Cu^{2+} and Fe^{2+} because of their low solubility. The formation of ferric arsenate has become the most important process, and its precipitation, solubility, and stability has been the subject of considerable research. Due to the unique characteristics of each plant operation, it is difficult to realize a comparison between the different arsenic treatment processes. A survey was carried out to provide information that could be useful in the complex arsenic treatment industry.

The present work covers the following topics: Arsenic and Its Compounds, Arsenic Distribution in Copper Smelters, Arsenic in the Chilean Copper Industry, Arsenic Recovery Worldwide and Arsenic Disposal from Metallurgical Processes.

Chapter 2 entitled "Arsenic and Its Compounds", a review is presented on the effects of arsenic on human health, its effect on the properties of copper, its solution chemistry, its production, consumption and uses worldwide, ambient standards and guidelines, and techniques for analysis and removal of arsenic from drinking water. The factors affecting the distribution of arsenic in copper smelters are described in Chapter 3. Chapter 4 describes the environmental situation in the Chilean mining industry, regarding the regulations and present solutions for management of SO_2, particulate matter, and arsenic. Chapter 5 entitled "Arsenic Recovery Worldwide" analyses processes for arsenic recovery from gold, cobalt, and copper concentrates as well as from arsenic-containing copper smelter dusts. Arsenic disposal by hydrometallurgical and pyrometallurgical processes is analyzed in Chapter 6. Chapter 7 entitled "Summary of Arsenic Treatment Processes" summarizes the results of arsenic operations in industry (recovery or disposal) from copper, cobalt, and gold concentrates, and from copper smelter dust. Finally, Chapter 8 presents the conclusions of the work and recommendations for the management, recovery or disposal of arsenic residues in the metallurgical industry.

Since the author has examined a large number of publications which were not cited in the text, it was considered worth while to compile these as Appendix I.

CHAPTER II

ARSENIC AND ITS COMPOUNDS

2.1 Physical and Chemical Nature

Elemental arsenic is a metalloid that exists in a number of allotropic forms. Yellow arsenic, which volatilizes readily, is extremely poisonous. Gray arsenic, the ordinary stable form, exhibits low thermal conductivity and brittle. The semi-metallic form of arsenic is steel gray in color with a bright luster. It is very brittle and is a good conductor of heat but a rather poor conductor of electricity. It is believed that Albertus Magnus obtained the element in 1250. Arsenic occurs in the oxidation states, –III, 0, III, V. Only one stable isotope of arsenic having mass 75 has been observed. The physical properties of elemental arsenic are presented in Table 2.1.

Arsenic is found widely in nature, rarely in the elemental form, most often combined with oxygen and sulfur. It is usually found in sulfide ores containing gold, silver, cobalt, nickel, iron, copper, lead and antimony. There are over 180 known arsenic-bearing minerals (Gonzalez and Monhemius, 1988). Table 2.2 list some of the more common minerals.

Inorganic and organic arsenic compounds are typically white to colorless powders. Arsenic oxide can be extracted from the flue-dust of copper and lead smelters, which can then be reduced with charcoal to produce metallic arsenic. Table 2.3 presents a summary of the formulas and uses of the most commonly used arsenic compounds.

Table 2.1. Physical properties of elemental arsenic

Property	Value
Atomic number	33
Atomic weight	74.92 g
Melting point (at 28 atm)	817°C
Boiling point	613°C[a]
Specific gravity (26°C)	5,778 kg/m^3
Specific heat	24.6 J/(mol·K)[b]
Latent heat of fusion	27,740 J/(mol·K)[b]
Latent heat of sublimation	31,974 J/(mol·K)[b]
Linear coefficient of thermal expansion (20°C)	5.6 μm/(m·°C)
Electrical resistivity (0°C)	26μΩ/cm
Crystal system	hexagonal (rhombohedral)
Lattice constants (26°C, mm)	a = 0.376 c = 1.0548

[a] Sublimes.

[b] to convert to cal/(mol·K) divide by 4.184

Table 2.2. Common arsenic-bearing minerals

Mineral		Formula
Arsenides	Nickeline	$NiAs_2$
	Safflorite	$(Co,Fe,Ni)As_2$
	Skutterudite	$CoAs_3$
Sulfides and Sulfosalts	Arsenopyrite	$FeAsS$
	Arsenical pyrite	$Fe(As,S)_2$
	Cobaltite	$CoAsS$
	Enargite	Cu_3AsS_4
	Orpiment	As_2S_3
	Realgar	As_4S_4
	Tennantite	$(Cu,Fe)_{12}As_4S_{13}$
Oxides	Arsenolite	As_2O_3
	Claudite	As_2O_3
Arsenates	Oliverite	$Cu_2(AsO_4)OH$
	Scorodite	$FeAsO_4 \cdot 2H_2O$

Table 2.3. Formulas and uses of common arsenic compounds

Compound	Formula	Uses	Reference
Arsenic metal	As	Copper- and lead-based alloys, manufacture of crystalline GaAs	Reese, Jr., 1998
Arsenic disulfide	As_2S_2	Leather industry, depilatory agent, paint pigment, shot manufacture, pyrotechnics, rodenticide, taxidermy.	US EPA, 1998a
Arsenic pentasulfide	As_2S_5	Paint pigments, light filters, other arsenic compounds.	US EPA, 1998a
Arsenic thiorsenate	$As(AsS_4)$	Scavenger for certain oxidation catalysts and thermal protectant for metal-bonded adhesives and coating resins.	US EPA, 1998a
Arsenic trisulfide	As_2S_3	Pigment, reducing agent, pyrotechnics, glass used for infrared lenses, semiconductors, hair removal from hides.	US EPA, 1998a
Arsenic trioxide	As_2O_3	Pigments, decolorizing agent in glass, insecticide, herbicide, wood preservative (CAA, ACZA, FCAP, ACA), preparation of other arsenic compounds.	Reese, Jr., 1999, Leach, 1999, Ibach, 1999.
Arsenic acid	$H_3AsO_4{\cdot}0.5H_2O$	Manufacture of arsenates, glass ceramics, wood treating process.	Edelstein, 1996
Arsenic pentoxide	As_2O_5	Arsenates, insecticides, weed killer, colored glass, metal adhesives.	US EPA, 1998a
Arsenic pentafluoride	AsF_5	Doping agent in electroconductive polymers.	US EPA, 1998a
Arsenic trifluoride	AsF_3	Fluorinating reagent, catalyst, ion implantation source, and dopant.	US EPA, 1998a
Arsenic hydride (arsine)	AsH_3	Organic synthesis, military poison, doping agent for solid-state electronic compounds.	US EPA, 1998a
Arsenic tribromide	$AsBr_3$	Analytical chemistry, medicine.	US EPA, 1998a
Arsenic trichloride	$AsCl_3$	Intermediate for organic arsenicals (pharmaceuticals, insecticides), ceramics.	US EPA, 1998a

2.2 Arsenic in the Environment

Arsenic compounds are emitted naturally from many sources, e.g., volcanoes, forest fires, erosion from minerals deposits. However, the arsenic release originating from human activities, e.g., metal smelting, chemical production and use, coal combustion, waste disposal, pesticide application can cause substantial environmental contamination because of its toxicity. The greatest environmental concentrations of arsenic have been observed in air and soil around mining and smelting operations, whereas coal combustion distributes arsenic to the air in much lower concentrations over a wider area.

2.2.1 In Air

Arsenic released to air from natural and industrial sources exists in the form of particulate matter less than 2 μm in diameter and is usually a mixture of arsenite and arsenate. The residence time of arsenic bound particulate depends on particle size and meteorological conditions; however, a typical value is approximately 9 days (US EPA, 1998a). Levels of arsenic in air range from a few nanograms (ng) to a few tenths of a microgram per cubic meter ($\mu m/m^3$), however, concentrations may exceed 1 $\mu m/m^3$ near stationary sources of emissions (Bencko, 1987).

2.2.2 In Water

Arsenic found in surface water, groundwater, and drinking water is mainly arsenate generally between 1 and 2 μg/L (Health Canada, 1992). A few micrograms per liter (μg/L) of arsenic is normally found in drinking water. In some locations, however, concentrations may exceed 1 milligrams per liter (mg/L) (WHO, 1981).

Arsenic is released to water in several ways, including natural weathering processes, discharge from industrial facilities, and leaching from landfills, soil or urban runoff. Once in water, arsenic can undergo complex series of transformations, including oxidation-reduction reactions, ligand exchange, and biotransformations. The parameters that most strongly influence the transformations are the oxidation-reduction potential (Eh), pH, metal and sulfide ion concentrations, iron concentrations, temperature, salinity and distribution and composition of the biota. Aquatic microorganisms may reduce the arsenate to arsenite and a variety of methylated arsenical compounds. Arsenic can also be adsorbed from water onto sediments and soils, particularly clays, iron oxides, aluminum hydroxides, manganese compounds, and organic material (US EPA, 1998a).

2.2.3 In Soil

The majority of soils naturally contain about 7 ppm of arsenic, but levels in the range of 100-2500 ppm have been detected near stationary sources, and up to 700 ppm in agricultural soils treated with arsenic-containing pesticides (WHO, 1981). Organoarsenical pesticides (e.g., monosodium methanearsonate, disodium methanearsonate) applied to soils are metabolized by soil bacteria to form alkyl-arsine and arsenate. Arsenic will react with soil components predominantly by adsorption on hydrous iron and aluminum oxides. Heavier soils with a higher clay content and hydrous oxide content adsorb more arsenic than do lighter sandier soils with low clay content. In addition, arsenic compounds react with ions in solution, such as iron, aluminum, calcium, magnesium, manganese, and lead. The pH of the soil will affect the solubility of these compounds (US EPA, 1998a).

There are two known types of oxidation that are responsible for transforming arsenic compounds environmentally. One type destroys the carbon/arsenic bond and is associated with microbial activity, while the other type causes a change in oxidation state. Transformations of arsenic in soil are similar to those seen in aquatic systems, with As^{+5} predominant in aerobic soils; As^{+3} in slightly reduced soils (e.g., temporarily flooded); and arsine, methylated arsenic, and elemental arsenic in very reduced conditions (e.g., swamps and bogs). Some arsenate may be reduced to arsenite under certain environmental conditions. Arsenic in sediments or in flooded anaerobic soil may be reduced as a function of reduction/oxidation potential (US EPA, 1998a). Figure 2.1 shows the biological cycle of arsenic.

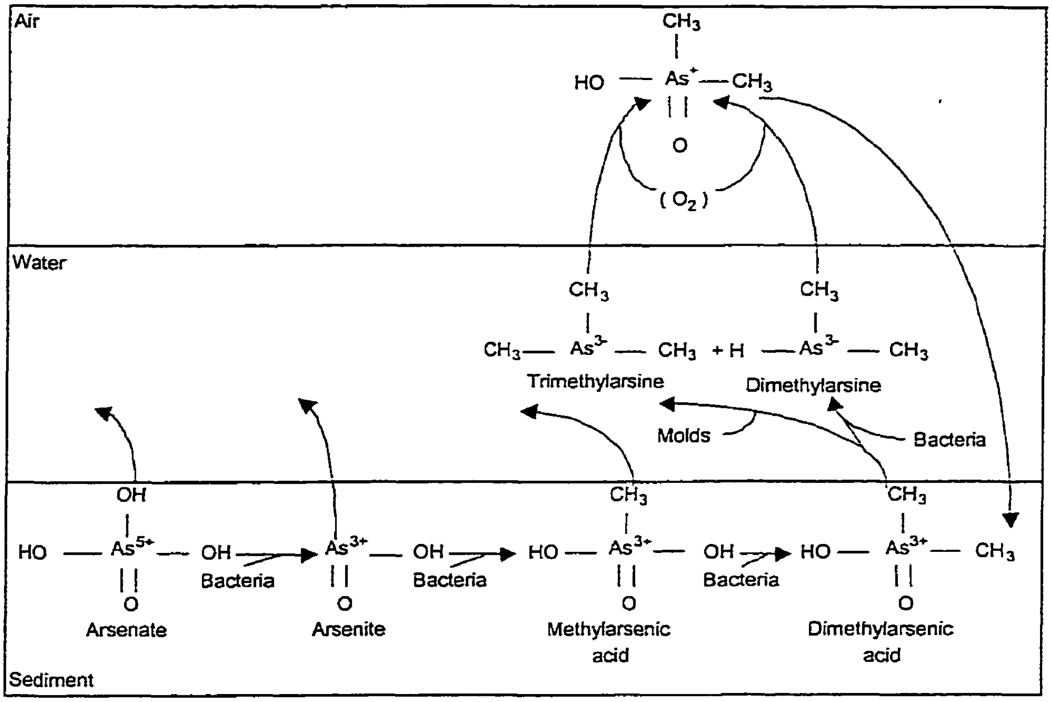


Figure 2.1. The biological cycle of arsenic (after Drever, 1997)

2.3 Arsenic and Human Health

2.3.1 Toxicity

All arsenic compounds are considerably toxic, especially the inorganic ones, and trivalent compounds are more toxic than pentavalent compounds.

2.3.2 Pharmacokinetics and Metabolism

Although the results of studies indicate that arsenic may be an essential element for several animal species (e.g., goats, minipigs, rats, chicks), there is no evidence that it is essential for humans. Humans are exposed to arsenic in many different ways: by ingestion of contaminated water and food; by ingestion of arsenic-containing medicinal preparations; by homicidal and suicidal ingestion of arsenicals; by inhalation of arsenic-containing dust or volatile arsenicals; and by absorption through skin and mucous membranes during the handling of arsenicals or through prolonged therapeutic usage in numerous professions. The most toxic arsenic compound, arsine (AsH_3), is an occupational hazard.

Ingested elemental arsenic is poorly absorbed and largely eliminated unchanged. Arsenic oxides are readily absorbed (>80%) from the gastrointestinal tract and, to a lesser extent, through the lungs and skin. According to some basic experiments in humans the absorption of soluble As (III) and As (V) compounds is close to 95%. Arsenic (III) tends to accumulate in the tissues, whereas As (V) and organic arsenic are well absorbed but rapidly and almost completely eliminated via the kidneys (Health Canada, 1992).

Following ingestion, inorganic arsenic appears rapidly in the circulation, where it binds primarily to haemoglobin; within 24 hours, it is found mainly in the liver, kidneys, lungs, spleen and skin. Skin, bone and muscle represent the major storage organs.

There are two main processes for the elimination of ingested trivalent arsenic from the body. The first is the rapid urinary excretion (close to 90% of the total urinary arsenic over the first 12-hour period). The second involves methylation of As (III) in the liver to monomethylarsenic acid (MMAA) and dimethylarsenic acid (DMAA), then excretion commences approximately five hours after ingestion but reaches its maximum level two to three days after. Less important routes of elimination of inorganic arsenic include skin, hair, nails and sweat (Health Canada, 1992).

2.3.3 Effect on Humans

In a 1980 review of arsenic, the International Agency for Research on Cancer (IARC) determined that inorganic arsenic compounds are skin and lung (via inhalation) carcinogens in humans. Many cases of skin cancer have been reported among people exposed to arsenic through medical treatment with inorganic trivalent arsenic compounds, particularly Fowler's solution (IARC, 1980).

The most deceptive and dangerous aspect of the arsenic toxicosis is its very slow and insidious development. After several years of continued low level of arsenic exposure, many skin ailments appear, i.e., hypopigmentation (white spots), hyperpigmentation (dark spots), collectively called melanosis, and keratosis (break up of the skin on hands and feet). After an exposure of about 10 years, skin cancers appear. After an exposure of 20-30 years, internal cancers, particularly bladder and lung appear (Mizanur, 1999). Signs of arsenic toxicosis, including dermal lesions, peripheral neuropathy, skin cancer, peripheral vascular disease and possibly cancers of other organs, have been observed in populations ingesting arsenic-contaminated drinking water in Taiwan, Chile, the United States, Mexico, and Canada. Dermal lesions, such as hyperpigmentation, warts and keratosis of the palms and soles, were the most commonly observed symptoms, occurring after minimum exposure periods of approximately five years (Health Canada, 1992).

In Chile, numerous adverse effects, particularly among children, have been associated with the consumption of arsenic-contaminated water in Antofagasta (Borgono and Greiber, 1971; Zaldívar, 1980). Effects on the skin (leukomelanoderma, hyperkeratosis), respiratory system (chronic coryza, cough, bronchopulmonary diseases), cardiovascular system (myocardial infarction, peripheral vascular disorders such as ischaemia of the tongue, Raynaud's phenomenon, acrocyanosis) and digestive system (abdominal pain, chronic diarrhoea) were observed in children under 16 years of age. Smith, et al. (1998) investigated cancer mortality in a population of around 400,000 people in a region of Northern Chile (Region II) exposed to high arsenic levels in drinking water in past years. Arsenic levels reached 570 μg/L between 1955 to 1969, and decreased to less than 100 μg/L by 1980. The findings provided evidence that ingestion of inorganic arsenic in drinking water is indeed a cause of bladder and lung cancer.

Arsenic is also found in other villages near Antofagasta (e.i., San Pedro de Atacama, Toconao, Baquedano and Sierra Leona), where arsenic concentrations in drinking water is above the limit set for drinking water (0.05 mg/L), reaching to 0.8 mg/L in Chiu Chiu (La Tercera, 1999).

Cancer mortality was examined in relation to arsenic concentration in drinking water in the villages of the contaminated area of Taiwan (0.1 to 0.6 mg/L), which were significant dose-response relationships for age-adjusted rates of cancers of the bladder, kidney, skin and lung in both sexes and cancers of the prostate and liver in men (Health Canada, 1992).

But, the largest groundwater arsenic contamination has occurred in Bangladesh and West Bengal, because of the poisoning of potentially 70 million people from arsenic present in water drawn from about 4 million of wells installed to solve shortages of drinking water. Arsenic has been reported to derive from the oxidation of arsenic-rich pyrite in the aquifer sediments, which is oxidized by atmospheric oxygen caused by lowering of the water table, forming soluble arsenic-containing oxypyrites (Lepkowski, 1998), but this explanation is not consistent with the observations made in Bangladesh by a group headed by geologist Ross Nickson of University College, London. The authors believe the critical mechanism proceeds not in an oxygen environment but in an anoxic one, a condition to be expected at the depths to which wells are drilled (about 100 metres). They suggest that arsenic is released when arsenic-rich iron oxyhydroxides are reduced to the soluble state by organic matter simultaneously present in that sedimentary geology. The reduced material, when exposed to aquifer water, leaches the arsenic into solution and thereby produces the contamination (Nickson, et al., 1998).

Measured arsenic concentrations reach up to 1 mg/L, which is above the limit set for drinking water in Bangladesh (0.05 mg/L) or that recommended by the World Health Organization (0.01 mg/L) (Nickson, et al., 1998). To date, 4,000 cases of arsenicosis patients have been identified (Hussain, 1999). The number of cancer expected in Bangladesh from the exposure already undergone can be roughly estimated by assuming that there are 20 to 70 million exposed persons at levels between 0.05 mg/L and 0.5 mg/L. These estimates will vary between 200,000 and 2 million (Wilson, 1998).

Occupational exposure to inorganic arsenic, especially in mining and copper smelting, has quite consistently been associated with an increased risk of cancer (IARC, 1980). A number of studies about arsenic poisoning of smelter workers have been reported in the literature (Higgins, et al., 1981; Lee-Feldstein, 1983, 1986; Lubin, et al., 1981; Welch, et al., 1982). Sulphur dioxide in the smelter environment also appeared to play a minor role, if any, in the development of lung cancer (Welch, et al., 1982). Other forms of cancer were considered, but their incidences were not found to be consistently increased (Lee-Feldstein, 1983). Other US smelter worker populations have been shown to have consistent increases in lung cancer incidence, as well as increases of about 20% in the incidence of gastrointestinal cancer and of 30% for renal cancer and haematolymphatic malignancies (Enterline and Marsh, 1980, 1982). The observation in an earlier study of an increase in lung cancer risk among a population of Swedish smelter workers (IARC, 1980) has been confirmed, with a risk of six to eight fold among roasters (Wall, 1980).

A decrease in lung cancer risk after cessation of exposure to arsenic has been observed in some studies (Enterline and Marsh, 1980; Pinto, et al., 1978), possibly indicating a late-stage effect of arsenic (Brown and Chu, 1983a, 1983b). With regard to histological type of lung cancer, a significant, relative excess of adenocarcinomas and a slight excess of goat-cell cancers were seen among smelter workers (Wicks, et al., 1981). A multiplicative effect of arsenic exposure and smoking was observed among Swedish smelter workers (Pershagen, et al., 1981). A slightly increased risk was also indicated for exposure to sulphur dioxide in this study. Other studies have shown a lesser influence of smoking (Higgins, et al., 1981; Pinto, et al., 1978).

Regarding the environmental pollution caused by the metallurgical industry, heavy arsenic contamination in three lakes and in a nearby tailing pond have been found near Yellowknife City in Canada (CBC News, 1999a). The Giant mine was operated by Royal Oak Mines, an American company, but it was purchased in 1999 by Miramar Mining Corporation, a Canadian company. The agreement gave the company access to the mine's gold reserves, but Miramar did not inherit responsibility for existing environmental contamination (CBC News, 1999b). During the Giant mine operation about 270,000 tons of arsenic trioxide and 800,000 liters of waste petroleum products were stored underground at an abandoned gold mine. The cost to clean the Giant mine will be paid by federal and territorial taxpayers because the company is bankrupt (CBC News, 1999c). A report prepared for the territorial and federal governments estimates surface cleanup of Giant Mine will cost taxpayers at least $16.3 million (Northern News Services, 2000).

2.4 Effects on Copper Properties

The properties of the final copper product, such as castability and rollability, electrical conductivity and workability are affected by the impurities (e.g., arsenic) (Baboudjian, et al., 1995). Arsenic tends to form compounds at the grain boundaries during solidification and these may cause hot cracking under the stress of straightening and rolling the newly cast bar. Arsenic tends to lower the electrical conductivity of copper. Arsenic also adversely affects the properties of copper for a good workability, such as low annealing temperature, low hardness, low tensile strength, and a large elongation to failure. Impurities that form solid solutions of the substitutional type likewise increase hardness and tensile strength (Fabian, et al., 1997). Impurities that adversely affect the workability properties are As, Bi, Se and Te, they are difficult to oxidise and tend to stay in solid solution in copper (Adams and Sinha, 1990).

2.5 Solution Chemistry of Arsenic

Arsenic chemistry is complex, involving a variety of oxidation states, anionic and cationic species, and it occurs as both inorganic and organic compounds and these are all commonly found in solid arsenic wastes, often at the same time. The valency changes easily and reversibly with redox potential (Swash and Monhemius, 1998). Speciation in non-complexing solutions is described most conveniently by means of the potential – pH diagram shown in Figure 2.2. The aqueous species which are relevant to the hydrometallurgical precipitation of arsenic compounds are AsO^+ and H_3AsO_3 for arsenic (III) and H_3AsO_4 and $H_2AsO_4^-$ for arsenic (V).

Under oxidizing conditions, the dominant form of arsenic is the +V oxidation state, which is present as arsenic acid and its anions (arsenate), corresponding closely to phosphoric acid and phosphate species. Oxygen at elevated temperatures and pressures is used in hydrometallurgical processes for oxidation of arsenic (III) to arsenic (V). Other oxidizing agents which have been used are Fe (III), $NaClO_3$, MnO_2, $K_2Cr_2O_7$, H_2O_2 or HNO_3 (Robins, 1988).

As conditions become reducing, As (V) is reduced to As (III)- arsenious acid and arsenite anions. The difference in solubility between As_2O_3 and As_2O_5 is the basis for reduction of arsenic (V) to arsenic (III) in order to recover As_2O_3 in a number of industrial processes. For example, at 25 °C the solubility of As_2O_3 is 20.9 g/kg H_2O and of $As_2O_5 \cdot 4H_2O$ it is 1,141.5 g/kg H_2O (Robins, 1985a). The reduction of arsenic (V) to arsenic (III) is possible using sulfur dioxide, which is used to precipitate arsenic trioxide from arsenic acid solutions as a commercial commodity (Toyabe, et al., 1988). When sulfate reduction occurs, arsenic precipitates as sulfide. Elemental arsenic is a stable species under highly reducing conditions. Table 2.4 summarizes the inorganic speciation of arsenic according Eh/pH representation (Sracek, A., 1998).

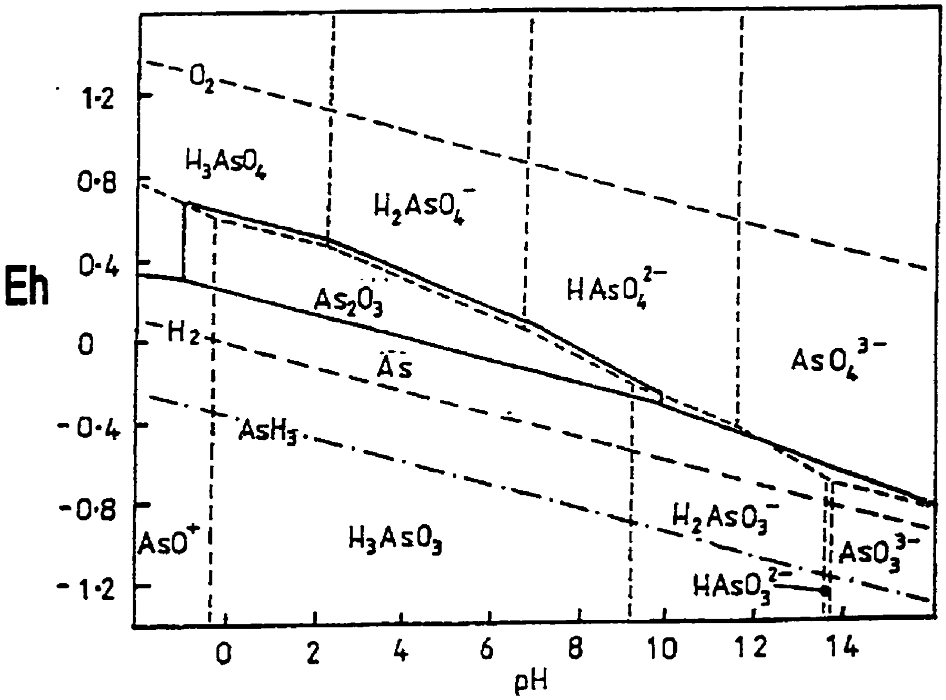


Figure 2.2. Eh–pH equilibrium diagram for the system arsenic – water at 25°C and at unit activity of all species (Robins, 1988).

Table 2.4. Inorganic speciation of arsenic

Eh/pH	Very acid	Acid	Basic	Very basic
Oxidized, Arsenic as As (V)	H_3AsO_4 Precipitation of $FeAsO_4 \cdot 2H_2O$ Scorodite, to $pH \cong 1.5$	$H_2AsO_4^-$	$HAsO_4^{2-}$ pH: 7.0 - 11.5	AsO_4^{3-} for $pH > 8.3$ precipitation of $Ca_2AsO_4(OH)$
Reduced, Arsenic as As (III)	H_3AsO_3	H_3AsO_3	H_3AsO_3 $H_2AsO_3^-$, for $pH > 9.2$	$HAsO_3^{2-}$ for $pH > 12.1$, for $pH > 8.3$ precipitation of $CaAsO_2(OH)$
Strongly reduced, Arsenic as As (III)	Precipitation of As_2S_3	Precipitation of As_2S_3	$As_2S_2^-$	$As_2S_2^-$

2.5.1 Solubility and Stability of Arsenic Compounds

During pyrometallurgical processes of arsenic-containing ores or concentrates some of the arsenic inevitably reports to the final effluents, which have to be stabilized prior to disposal. The disposal of arsenic has been accomplished in practice by the formation of metal arsenates and metal arsenites, e.g., of Ca^{2+}, Cu^{2+} and Fe^{2+} because of their low solubility.

In 1956 Chukhlantsev was the first researcher to perform a comprehensive study on the solubility of metals arsenates. He showed that the solubility of the metal arsenates is considerably lower than that of the corresponding arsenites, and hence the arsenates are of more interest in hydrometallurgy (Figure 2.3). This figure shows an extremely low solubility for barium arsenate and mercurous arsenate. Both of these arsenates are in fact almost five orders of magnitude higher than Chukhlantsev's reported values. The insolubility of barium arsenate was the basis of a patent for arsenic removal (Weir and Masters, 1980). There is, however, some dispute about this low solubility figure and about the possible reaction of barium arsenate with CO_2, as a result the solubility re-determined by Robins in 1985b.

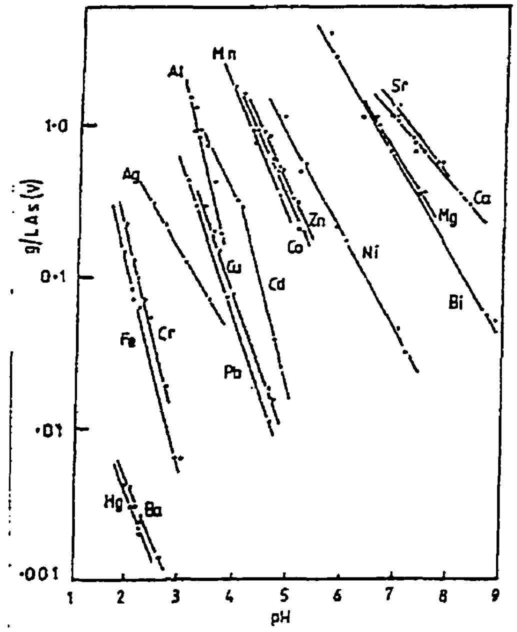


Figure 2.3. The solubility of various metal arsenates taken from the work of Chukhlantsev (Robins, 1988)

Arsenic has been precipitated by adding lime to the solution, obtaining a calcium arsenate compound:

$$3CaO + 6H^+ + 2AsO_4^{3-} \rightarrow Ca_3(AsO_4)_2 + 3H_2O \qquad (2.1)$$

However, the stability of this compound has been questioned because under the influence of CO_2 in the air, calcium arsenate decomposes to calcium carbonate and liberates arsenic oxide in the solution (Nishimura, et al., 1985, 1988):

$$Ca_3(AsO_4)_2 + 3CO_3^{2-} \rightarrow 3CaCO_3 + 2AsO_4^{3-} \qquad (2.2)$$

Robins and Tozawa (1982) have pointed specifically to this problem; the potential ineffectiveness of lime in removing arsenic from gold processing waste waters. Also, solution pH exerts a strong influence on arsenate solubility as indicated by the data shown in Figure 2.4 from which it can be seen that calcium arsenate reacts with CO_2 to liberate arsenic in solution and this prevents the prcipitation of calcium arsenate (Terry, 1992).

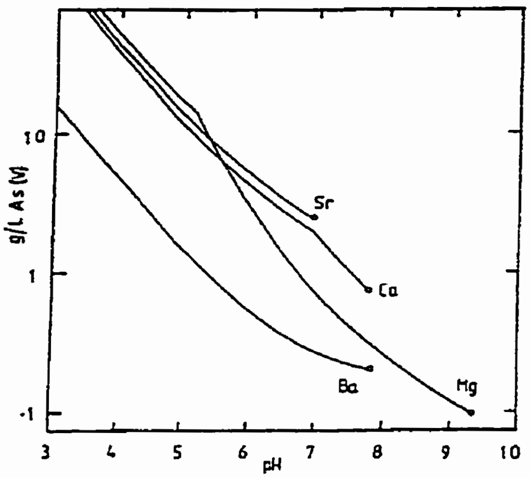


Figure 2.4. The solubility of arsenates of calcium, barium, magnesium, and strontium. (Robins, 1988)

For a long term stability, the formation of more stable forms has been studied (i.e., Cu, Zn, Co, Ba, Hg, etc.) (Tozawa, et al., 1977, 1978; Robins, 1981, 1982, 1984; Tozawa and Nishimura, 1984), but at present the industry has adopted the ferric arsenate method known as scorodite. According to Eh-pH diagrams of the Fe-As-H_2O system (Figures 2.5 and 2.6), it is possible to form a ferric arsenate ($FeAsO_4 \cdot 2H_2O$) from arsenic (V) and iron (III) forms.

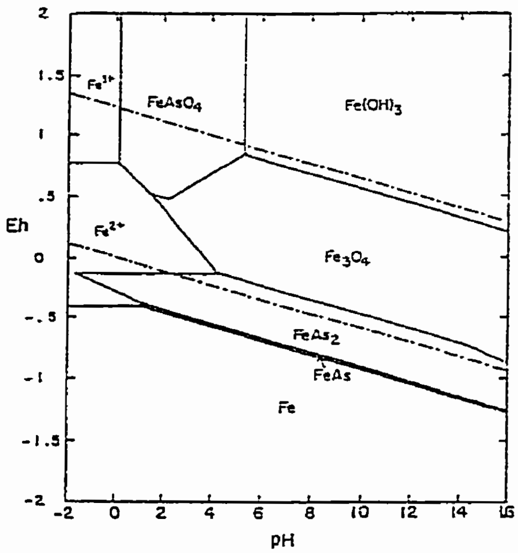


Figure 2.5. The Eh-pH diagram of the Fe-As-H_2O system showing iron compounds at 25°C and at unit activity for all species (Mirza, et al., 1988).

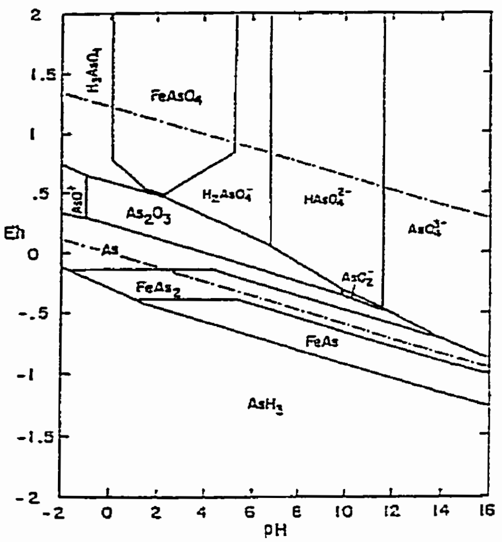


Figure 2.6. The Eh-pH diagram of the Fe-As-H_2O system showing arsenic compounds at 25°C and at unit activity for all species (Mirza, et al., 1988).

Ferric arsenate has been reported in the literature over many years (Robins, 1985a, 1988; Krause and Ettel, 1987, 1989). According to Droppert (1996), there are two kinds of ferric arsenate. The first kind is amorphous and it has the empirical formula $Fe_xAsO_4(OH)_{3(x-1)}$ where x has to be 4 or more in order to have an insoluble compound. All these precipitates are called "basic ferric precipitates". The second ferric arsenate is the mineral $FeAsO_4 \cdot 2H_2O$, scorodite, which is crystalline and has a Fe/As ratio of 1.0.

On the other hand, ferrous arsenate has also shown to be insoluble (Figure 2.7) but due to the eventual oxidation of Fe (II) to Fe (III) by atmospheric O_2 and the difficulty of producing it, do not seem to offer a particular advantage over ferric arsenate as a solid waste compound (Terry, 1992).

The two sulfides As_2S_3 and As_4S_4 (corresponding to the minerals orpiment and realgar, respectively) have low solubility in acidic solutions, where the solubility curves are terminated at the point of incongruent solubility in respect to hydroxide or carbonate compounds formation (Figure 2.7). However, their use is not favored because of the possibility of atmospheric and bacterial oxidation liberating arsenic (Terry, 1992).

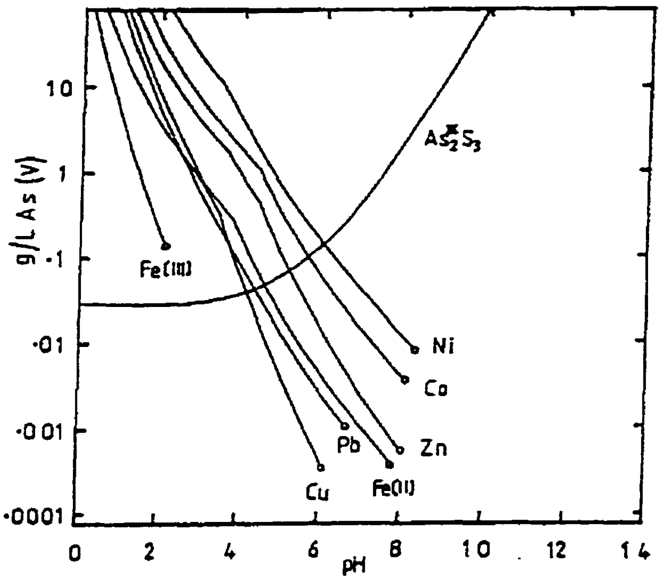


Figure 2.7. The solubility of various metal arsenates and arsenic (III) trisulfide taken from recent works. (Robins, 1988).

Twidwell, et al. (1995) investigated the stability and solubility of $Ca_3(AsO_4)_2$. They noted that the solubility decreased one to two orders of magnitude over the range of pH 9-12.6, in the presence of phosphate ions (Table 2.5).

Table 2.5. Influence of solution pH on precipitate solubility (after Twidwell, et al., 1995)

System	Concentration, µg/L		
	pH = 9.0	pH = 10.0	pH = 12.6
Ca-As	70,075	10,800	19.0
Ca-As-P	1,445	57.0	0.5

2.5.1.1 Ferric Arsenate

As previously stated, the favored precipitate for arsenic removal is a ferric arsenate, and the precipitation, solubility, and stability have been the subject of considerable research. On one hand, this was due to the environmental considerations and on the other due to the controversy related to the solubility of them. Here are recent results from this subject.

- **Formation of amorphous ferric arsenate**

Direct neutralization of hydrometallurgical solutions containing Fe(III) and As(V) leads to the production of amorphous precipitates or $Fe(III)_x$-As(V)-OH_y sludges. If the molar ration Fe/As is 1 then these precipitates forms whole minimum solubility is in the interval 50 to 100 mg/L (Demopoulos, et al., 1994).

$$Fe^{3+} + H_2AsO_4^- + 2H_2O \rightarrow FeAsO_4 \cdot 2H_2O + 2H^+ \qquad (2.3)$$

In 1956 Chukhlantsev prepared ferric arsenate but measured only the iron concentrations in determining solubility in both sulfate and nitrate solutions. This introduced a large error, as was shown in 1978 by Nishimura and Tozawa, who determined the solubility of ferric arsenate by measuring iron (III) and arsenic (V) concentrations. They showed that the Fe:As ratio deviated from unity above pH ≈ 2 (Figure 2.8). This was described by Robins in 1981 as being due to incongruent dissolution and the formation of ferric hydroxide (Figure 2.9). Thus at pH lower than 2 the following equilibrium would occur (Droppert, 1996):

$$FeAsO_4 \cdot 2H_2O + 3H^+ \Leftrightarrow Fe^{3+} + H_3AsO_4 + 2H_2O \qquad (2.4)$$

From pH ≈ 2 to pH ≈ 6 this reaction will shift to:

$$FeAsO_4 \cdot 2H_2O \Leftrightarrow H_2AsO_4 + FeOOH + H^+ \qquad (2.5)$$

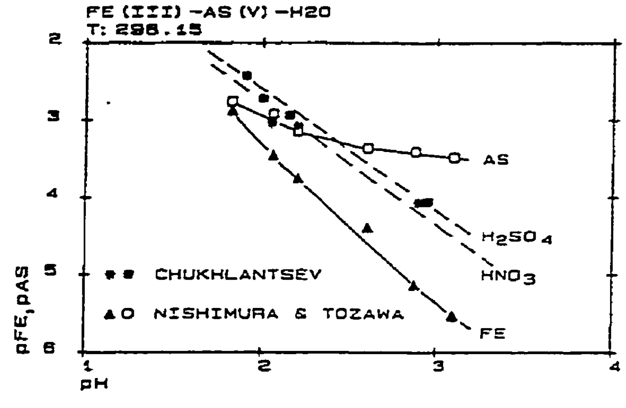


Figure 2.8. Solubility data for ferric arsenate from Chukhlantsev and Nishimura and Tozawa (Robins, 1990).

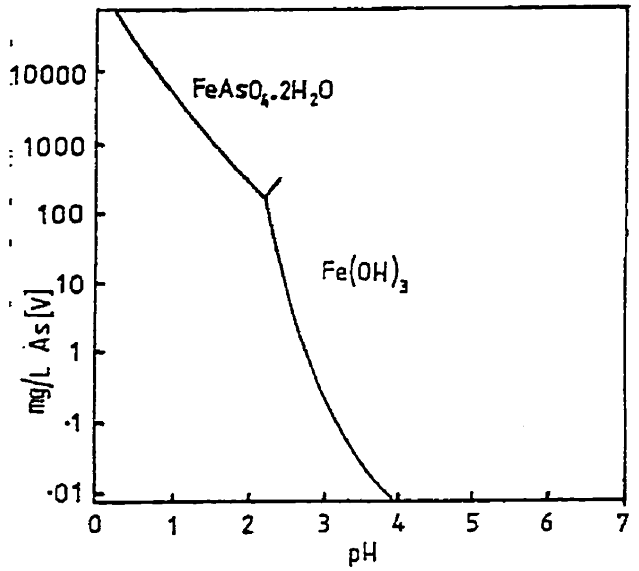


Figure 2.9. Solubility regions for ferric arsenate and amorphous ferric hydroxide showing the point of incongruent solubility at about 150 mg/L arsenic (Robins, et al., 1988).

Later, Krause and Ettel (1985, 1987) found that the molar Fe:As ratio has an effect on the solubility of precipitated arsenic-containing ferric hydroxides (Figure 2.10) and that the presence of CO_2 do not increase the solubility of arsenic. They showed that a minimum molar Fe:As ratio of 4 is required in the solution to favor the formation of an amorphous ferric arsenate of lower solubility (< 1 mg/L in the pH range 3–7). The authors called these high Fe:As ratio precipitates “basic ferric arsenates”, in analogy to the basic ferric sulfates, with the formula $FeAsO_4 \cdot 3Fe(OH)_3$ or $Fe_4(AsO_4)(OH)_9$. Other work by Harris and Monette (1988) and Papassiopi, et al., (1988) show a similar trend in the variation of the Fe:As ratio. This process is effective for low arsenic-containing effluent. However for the fixation of arsenic in As-rich solution or flue dust, the application of this method would lead to the generation of a large volume of amorphous arsenic-bearing ferrihydrite/gypsum sludge because of the necessity to attain Fe/As molar ratio > 4 for sale disposal of it, having associated the following problems:

- Large amount of iron source and neutralizing agents
- The difficulty of liquid/solid separation
- Construction of big tailings pond for disposal

Over the long term they are expected to undergo aging and conversion to crystalline phases because that they are amorphous.

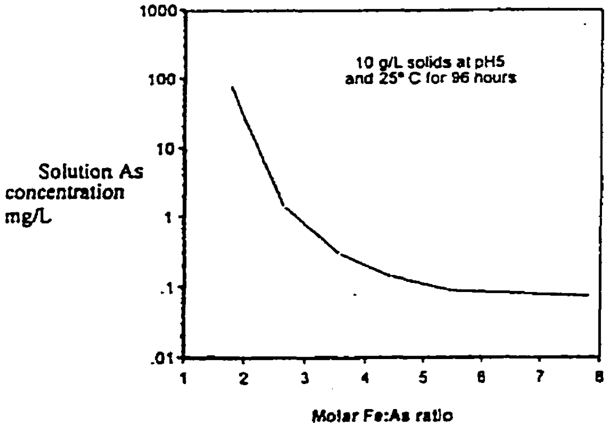


Figure 2.10. Arsenic solubility as a function of molar Fe:As ratio in amorphous ferric arsenate (after Swash and Monhemius, 1998).

Krause and Ettel (1989) have also established that crystalline ferric arsenate known in the nature as scorodite is approximately 100 times less soluble than amorphous ferric arsenate reported in the literature (Figure 2.11). Robins (1990) confirmed these results.

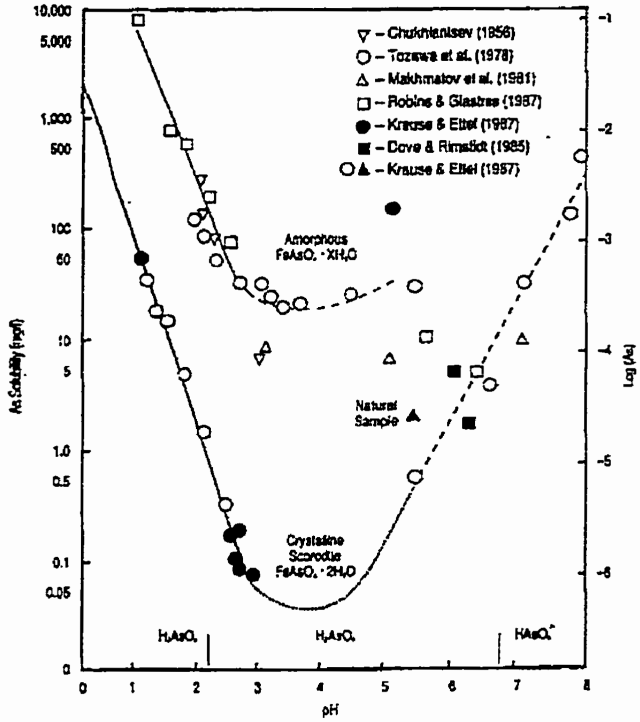


Figure 2.11 Comparison of As (V) solubility data for crystalline and amorphous ferric arsenate at 23°C (Krause and Ettel, 1989).

- **Formation of crystalline ferric arsenate**

Crystalline ferric arsenate, $FeAsO_4 \cdot 2H_2O$, known in nature as scorodite, is generally accepted as the most suitable compound for arsenic disposal, due to:

1. Its high arsenic content (stoichiometrically 32.47%).
2. It does not require a high Fe/As molar ratio in the starting solution.
3. It has a lower arsenic solubility (typically < 1 ppm As at pH = 5.0).

- Autoclave conditions at 150°C

Scorodite has been synthesized during jarosite precipitation at 150°C from sulfate solutions by Dutrizac, et al. (1987) obtaining complete arsenic precipitation for solutions containing 5 g/L As(V). Precipitation of scorodite in the Fe-AsO_4-SO_4 system at pH<1 was carried out in the temperature range 150-225°C ranging Fe/As molar ratio between 1:1 to 9:1 and precipitating

90% or of arsenic (Swash and Monhemius, 1994, 1998). The formation conditions in all these cases relate to the use of autoclaves, which are considered to being a capital-intensive technology.

- Ambient pressure at 95°C

Immobilization of arsenic in As(III)-rich chloride and sulfate solution and flue dust as scorodite by ambient aqueous oxidation (95°C) using H_2O_2 has been tested at McGill University by the Hydrometallurgy Group (Demopoulos et al., 1994, Droppert, 1996; Filippou and Demopoulos, 1997). Aqueous oxidation of As(III) with SO_2/O_2 gas mixture at a pH below 1.5 and the precipitation of scorodite with goethite residues has been reported by Qiankun and Demopoulos (1998). The approach developed at McGill University involves supersaturation control by a neutralization technique to avoid precipitation of any amorphous arsenic compounds. Precipitation of crystalline scorodite (Figure 2.12) is induced by the addition of scorodite seed material into the arsenic-rich solution, slow rate of addition of Fe^{3+}, where it never must be in excess. Thus, ≈ 90% of arsenic precipitates for solutions containing between 5 to 10 g/L As(V).

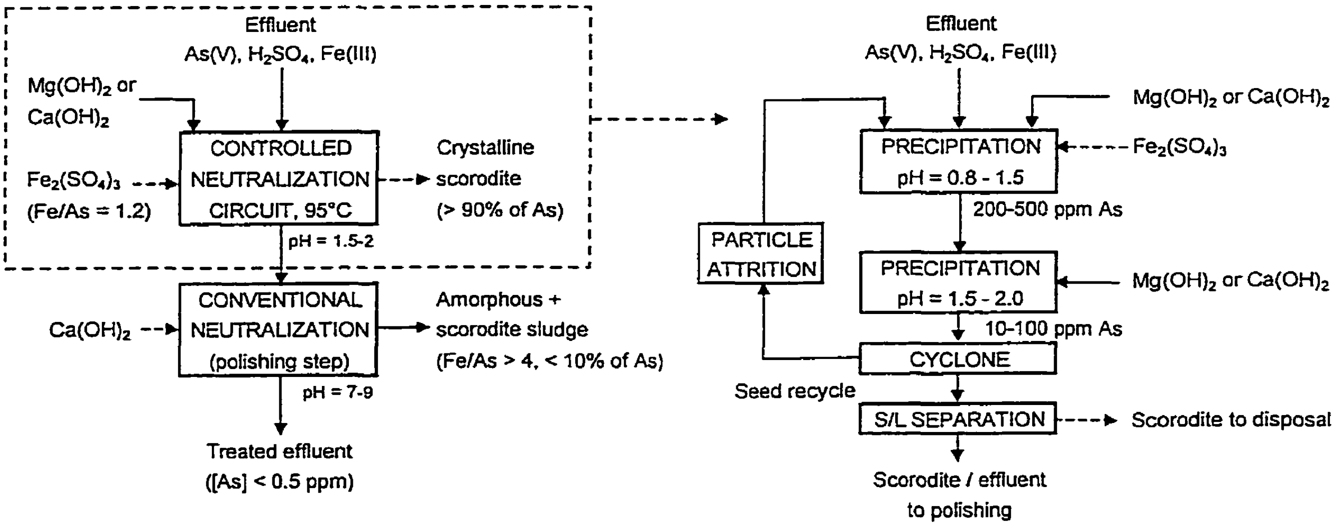


Figure 2.12. Schematic flowsheet of treatment of arsenic(V)-bearing effluents by scorodite precipitation (after Droppert, 1996).

Moreover, Robins (1990) has proposed that the compound $FeAsO_4 \cdot 2H_2O$ is expected to decompose in contact with water at pH > 5 on a long term basis and slowly release arsenic ions (Figure 2.13). But it will occurs if a closed system is considered. The particle size is an important factor in this case according to the Gibbs-Thomson effect, where the size of the individual particles influences the solubility of small crystalline particles, principally in the range of 10-100 nm (Demopoulos, et al., 1994).

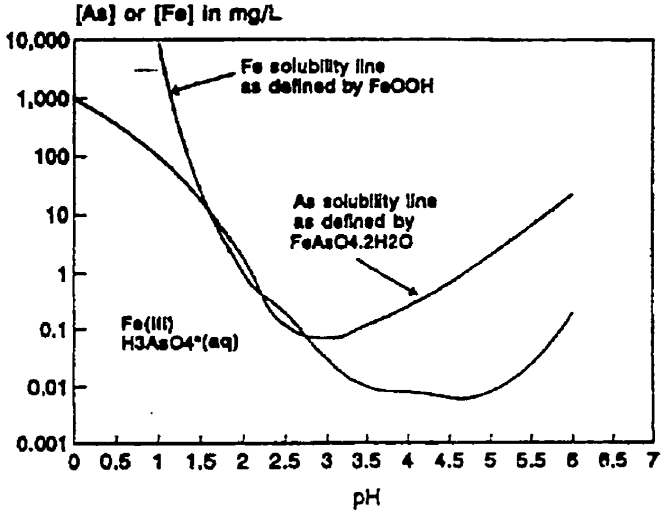


Figure 2.13. Solid-liquid equilibria in the Fe (III) – As (V) – H_2O system (Demopoulos, et al., 1994)

In summary it has been established that crystalline ferric arsenate known as scorodite has lower solubility than the amorphous ferric arsenate and high temperatures favor its precipitation. Different processes utilizing this material as an arsenic disposal carrier will be analyzed by the author in the chapter 6.

Solubility is not necessarily an indicator of long term stability; one should also take into account the physical and chemical changes that the compounds can undergo with time. The disposal and long term stability of arsenical materials can be examined indirectly by the study of naturally occurring arsenic materials and weathering products under natural conditions. For example, scorodite is the most common arsenate mineral and can be considered to be one of the most stable arsenic-bearing compounds. The broad range of climates in which scorodite is found, together with the wide variety of geological environments, reflects its stability (Swash and Monhemius, 1998).

2.6 Analytical Techniques for the Measurement of Arsenic

Atomic Absorption Spectroscopy (AAS) is commonly used for measuring total arsenic in samples (US EPA, 1998b). Samples of other than drinking water must be acid-digested prior to analysis. Three types of AAS methods for measuring total arsenic are direct aspiration (flame), graphite furnace, and hydride-generation. The second most common technique for measuring total arsenic in samples is Inductively Coupled Plasma, which allows simultaneous, or sequential, determination of several metals in a sample during a single analytical measurement. Samples must be acid-digested prior to analysis.

2.6.1 Direct Aspiration Atomic Absorption Spectroscopy

Method 7000A specifies the procedure for analyzing samples using direct-aspiration (flame) AAS. The typical detection limit for arsenic using this method is 0.002 (mg/L) (US EPA, 1998b). In this method, a sample is aspirated and atomized in an air/acetylene flame. A light beam from a hollow cathode lamp, whose cathode is made of the element being measured, is directed through the flame into a monochromator, and onto a detector that measures the amount of light adsorbed. Adsorption depends upon the presence of free, unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the element being measured, the light energy absorbed by the flame is a measure of the concentration of that element in the sample. With flame, if the proper flame and analytical conditions are not used, chemical and ionization interferences can occur. Flame AAS in normally performed as a single element analysis.

2.6.2 Graphite Furnace Atomic Absorption Spectroscopy (GFAA)

Method 7060A specifies the procedure for analyzing samples for total arsenic using graphite furnace AAS (US EPA, 1998b). This method is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. The typical detection limit for water samples using this method is 1 μg/L. This detection limit may not be achievable when analyzing waste samples.

The principle of graphite furnace AAS is essentially the same as for direct-aspiration AAS, except that a furnace rather than a flame is used to atomize the sample. In graphite furnace AAS, a representative aliquot of a sample is placed in a graphite tube in the furnace, evaporated to dryness, charred, and atomized. The radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. The atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected sample to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation. The advantage of GFAA is that it affords low detection limits. It is the easiest technique to perform on relatively clean samples. Because this technique is so sensitive, however, interferences can be a problem; finding the optimum combination of digestion, heating times, and temperatures, and matrix modifiers can be difficult for complex matrices.

2.6.3 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP)

Method 7300 specifies the procedure for analyzing samples using ICP (NIOSH, 1994a). The typical detection limit for arsenic using this method is 0.035 mg/L. The method measures element-emitted light by optical spectrometry. The sample is nebulized and the resulting aerosol is transported to the plasma torch, where excitation occurs. Characteristic atomic-line emission spectra are produced by radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer.

This method allows simultaneous or rapid sequential determination of many elements in a short time. The disadvantage is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult.

2.6.4 Hydride Generation Atomic Adsorption Spectroscopy (HGAA)

Method 7061A specifies the procedure for analyzing samples for total arsenic using HGAA (US EPA, 1998b). The typical detection limit for this method is 0.002 mg/L. It utilizes a chemical reduction to reduce and separate arsenic selectively from a digested sample along with standard AAS techniques. The advantage of this technique is that arsenic can be isolated and determined from complex samples. A disadvantage is that interferences will occur when easily reduced metals are present, and/or when high concentrations of transition metals are present. Also, oxidizing agents, such as oxides of nitrogen, may remain after the sample has been digested.

2.6.5 Ion Chromatography (IC)/GFAA

NIOSH Method 5022 specifies the procedure for analyzing air samples for total arsenic using an IC connected to GFAA. The working range is 0.005 to 10 mg/m^3 (as As) for a 100-L air sample. The method is designed to determine particulate organo-arsenic compounds (NIOSH, 1994b). It is a separation technique used for the analysis of ionic species. Separation of components in a sample can be achieved with the use of a mobile phase (eluent), and a stationary phase (a specific type of polymeric resin bed inside a column). A sample is introduced into the flowstream of the mobile phase (eluent) and is carried onto the stationary phase (column). The sample then undergoes a separation process based on its affinity for either of the mobile or stationary phases. With NIOSH Method 5022, the IC detector is bypassed, and the sample flows into an arsine generator where gaseous arsines are formed. A gas-liquid separator is then used to flow the sample into the GFAA where the sample is determined.

2.7 Production, Consumption and Utilisations of Arsenic

2.7.1 Production

Arsenic is recovered as a by-product of processing certain complex ores that are mined mainly for copper, lead, zinc, cobalt, gold, and silver, and its supply is dependent on the demand for these metals. In general, arsenic is regarded as a troublesome impurity in smelting and refining, and thus high-arsenic ores may be penalized at the smelter and refinery or avoided at the mine. World resources of copper and lead contain about 11 million metric tons of arsenic. Substantial resources of arsenic occur in copper ores in northern Peru, Chile and the Philippines and in copper-gold ores in Chile. In addition, world gold resources, particularly in Canada, contain substantial resources of arsenic (Resse, Jr., 1999).

Arsenic trioxide is the principal commercial arsenic compound. It has been produced in China for 500 years in extremely simple plants, consisting of retorts with condensation chambers, from an ore containing 15% As. However, the first smelter for native arsenic was set up at the beginning of the 18th century in Germany by of J.V. Scharfenberg in Reichenstein, Silecia. Because the demand for As_2O_3 was relatively low, it was not until 19th century that a second country, Great Britain, began producing As_2O_3. Thereafter, from the middle of the 19th century to 1901, Great Britain was the leading As_2O_3 producer. When legislation was introduced in various countries to avoid damage caused by release of As_2O_3 containing fumes, world production of As_2O_3 increased considerably. Also, the use of calcium arsenate to combat the boll weevil (insect which infested the cotton fields) in Mexico and the United States generated a demand for arsenic so great that it exceeded supply (Grossman, et al., 1997). New plants were established near the beginning of the 20th century, particularly in the United States and Mexico. The first arsenic production of the United States was a by-product of the smelting of gold and silver ores (USGS, 1999). The largest plant was operated between 1932 and 1991 by Boliden AB in Rönnskär, Sweden, which shut down permanently, reportedly for environmental reasons (Loebenstein, 1992).

The world production of arsenic trioxide has been falling steadily since 1974 (Figure 2.14), because it is a by-product, and production is determined not by the demand for arsenic but by the demand for copper, gold, lead, etc. However, despite environmental regulation that has led to the cessation of production in two historically large producing countries, Sweden (Boliden AB) and the United States (ASARCO Inc.), new suppliers have emerged to keep the world production.

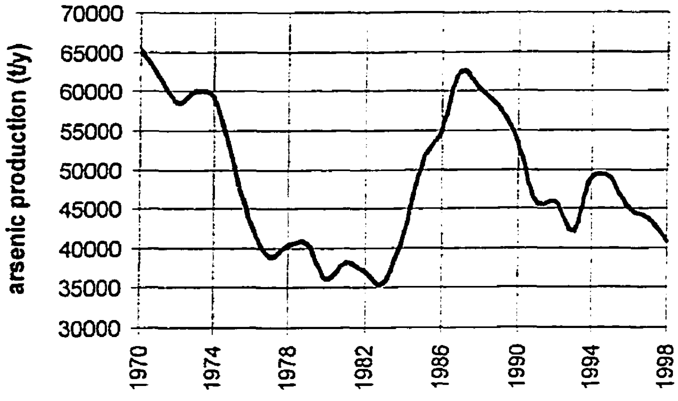


Figure 2.14. Arsenic production in tons of As_2O_3 content

In the past years, arsenic trioxide has been recovered from the smelting or roasting of nonferrous metal ores, concentrates or copper smelter dusts in at least 18 countries with China, France, Chile, Ghana, Mexico, Morocco, Namibia, Philippines, and Belgium being the major producers. However, most countries do not report their arsenic production and world production values have a high degree of uncertainty. In 1998, U.S. Geological Survey estimated the arsenic trioxide production at about 41,000 metric tons. China was the world's largest producer as well as the major source of U.S. imports (Reese, Jr., 1999). Chile could be in the near future the world's largest producer due to environmental regulations that limit the arsenic emitted to the atmosphere from smelters. The main countries producing arsenic trioxide in the last years are shown in Table 2.6, (Edelstein, 1994, 1995, 1996; Resse, Jr., 1997, 1998).

Table 2.6. World arsenic trioxide production (1,2,3)
(Metric tons)

Country	1990	1991	1992	1993	1994	1995	1996	1997	1998 e/
Belgium e/	3,000	2,500	2,000	2,000	2,000	2,000	2,000	2,000	1,500
Bolivia	300	463	633	663	341	362	255	282	290
Canada e/	485	236	250	250	250	250	250	250	250
Chile	5,830	6,820	6,016	6,200	4,050	4,076	8,000	8,350	8,400
China e/	9,000	10,000	15,000	14,000	18,000	21,000	15,000	15,000	15,500
France e/	6,480	2,000	2,000	3,000	6,000	5,000	3,000	2,500	2,000
Georgia e/	XX	XX	1,500	1,000	500	400	400	400	400
Germany 4/ e/	360	300	300	300	300	250	250	250	250
Ghana 5/	–	500	500	902	3,897	4,409	5,443	4,577	5,000
Iran e/	382	552	492	500	500	500	500	500	500
Japan e/	500	500	50	40	40	40	40	40	40
Kazakhstan e/	XX	XX	2,000	2,000	1,500	1,500	1,500	1,500	1,500
Mexico	4,810	4,920	4,293	4,447	4,400	3,620	2,942	2,999	3,000
Namibia 6/	1,640	1,800	2,456	2,290	3,047	1,661	1,559	1,232	300
Peru 7/ e/	500	661	644	391	286	285	285	285	285
Philippines e/	5,090	5,000	5,000	2,000	2,000	2,000	2,000	2000	2000
Portugal e/	200	200	150	1,50	150	100	100	50	50
Russia e/	XX	XX	2,500	2,000	1,500	1,500	1,500	1,500	1,500
Sweden 8/	7,000	2,500	–	–	–	–	–	–	–
U.R.S.R. 9/	7,800	7,000	XX	XX	XX	XX	XX	XX	XX
Total	**53,400**	**46,000**	**45,800**	**42,100**	**48,800**	**49,000**	**45,000**	**43,700**	**40,800**

e/ Estimated. XX Not applicable.

1/ Including calculated arsenic trioxide equivalent of output of elemental arsenic and arsenic compounds other than arsenic trioxide where inclusion of such materials would not duplicate reported arsenic trioxide production.

2/ World totals and estimated data are rounded to three significant digits; may not add to totals shown.

3/ Table includes data available through March 3, 1999. Austria, Hungary, the Republic of Korea, South Africa, Spain, the United Kingdom, the former Yugoslavia, and Zimbabwe have produced arsenic and/or arsenic compounds in previous years.

4/ All production for Germany in 1990 came from the former Western states.

5/ Estimated commercial byproduct of gold ore roasting. Does not include additional byproduct production of noncommercial grade material estimated at 4,000 tons in 1992, and up to 9,000 tons per year in 1993-96.

6/ Output of Tsumeb Corp. only. Tsumeb Mine closed in 1996, and the smelter and all operations closed in April, 1998.

7/ Output of Empresa Minera del Centro del Perú (Centromín Perú) as reported by the Ministerio de Energía y Minas.

8/ Based on arsenic trioxide exported plus the arsenic trioxide equivalent of the output of metallic arsenic exported.

9/ Dissolved in Dec. 1991.

Another arsenic compound is commercial-grade (99% pure) arsenic metal, which is produced through the reduction of arsenic trioxide. It is believed that China accounted for nearly all the world's production of commercial-grade arsenic metal. High-purity arsenic, 99.9999% or greater, is also produced for use in the semiconductor industry (Reese, Jr., 1998). Table 2.7 summarizes the principal world refiners of arsenic by country.

Table 2.7. Principal world refiners of arsenic

Country	Commodity	Source	Company	Production t/y, c/	Reference
Belgium	As_2O_3		Union Miniere S.A.	1,000	www.um.be
Bolivia	As_2O_3 As_2S_3	Mine output	Empresa Metalúrgica Vinto (subsidiaria de la Corporación Minera de Bolivia)	N.A.	Velasco, 1997a
Chile	As_2O_3	Cu-Au conc.	Barrick Gold Corp.	8,350	Velasco, 1997b
China	As_2O_3	Arsenic ore	Shui Kou Shan Mining Bureau 4/	N.A.	http://www.sksc.com/english/index.htm
	Arsenic metal (99.9%)				Zeping, 1999
	As_2O_3 (99.5%)	Cu conc.	Guixi Smelter, Jiangxi Copper Company		
Georgia	Arsenic	Mine output	Lukhumi deposit and Tsana deposit	2,000	Levine, 1996a
	Metals and compounds		Racha mining and chemical plant	NA.	
			Tsana mining and chemical plant	NA.	
Germany	High purity arsenic	As_2O_3	Preussag AG	15	Edelstien, 1996
Ghana	As_2O_3	Gold ore	Ashanti Goldfields	5,500	Coakley, 1997
France	As_2O_3 (99.9%)	Crude As_2O_3 from Ghana	Société minière et métallurgie de Penarroya	N.A.	Edelstien, 1996
			Metaleurop SA	3,000	Edelstien, 1994
Japan	As_2O_3 (99.9%)	Cu conc.	Sumitomo Metal Mining Co.	720	Terayama, 1999
	Arsenic metal	As_2O_3		18	
	High-purity arsenic (99.9999%)		Furukawa Electric Co. Ltd.	30	Edelstien, 1996
			Mitsubishi Metal Corp.		
			Rasa Industries Ltd.		
Kazakstan	As_2O_3		Chimkent polymetallic enterprise	1,500	Levine, 1996b
Morocco	As_2O_3	Co conc.	Omnium Nord Africain (ONA)	4,500	Private Communication from I. Akalay to F. Habashi dated 2000/2/11
Mexico	As_2O_3	Cu conc.	Industrial Minera Mexico SA (IMM)	N.A.	Torres and Doan, 1997
Namibia 1/	As_2O_3 (99%)	Cu conc.	Tsumeb smelter Corp.	1,800	Coakley, 1999
Peru	As_2O_3	Cu-Pb-Zn ores	Doe Run Resources Corp.	837	Gurmendi, 1998
Philippines	Arsenic, white	Cu conc.	Lepanto Consolidated Mining Co. 2/	2,000	Lyday, 1998
U. S. A.	High-purity arsenic, As_2Se_3	As_2O_3	Asarco, Globe CO plant	N.A.	www.asarco.com/products99/
	As_2O_3, arsenic metal		American Elements		www.americanelements.com/
			Hickson Corp.		www.hickson.com
	Arsenical wood preservatives		Chemical Specialities Inc.		Reese, Jr., 1998
	Arsenic acid		Osmose Wood Preserving		www.osmose.com
	Arsenical herbicide		ISK Bioscience		Reese, Jr., 1998

c/ Estimated. N.A./ Not available.

1/ Tsumeb Mine closed in 1996, and the smelter and all operations closed in April, 1998.

2/ Lepanto Consolidated Mining Co. closed its copper plant in 1997.

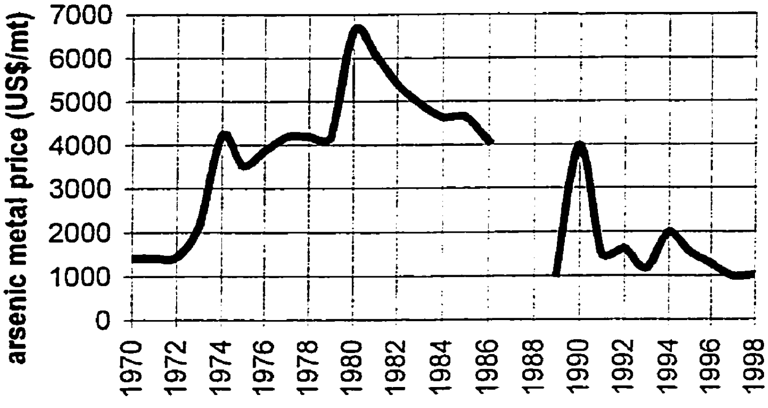
2.7.1.1 Prices

Price for arsenic trioxide is not available from world refiners. Although, some refiners as AllChem Industries gives on internet an arsenic trioxide price of US$680/mt (AllChem Industries, 2000). This price is some similar at the average prices for arsenic trioxide imported by the United States from Mexico in the last years (Table 2.8) (Edelstein, 1994, 1995, 1996; Resse, Jr., 1997). Normally, refiners quote two prices, one for high-grade (minimum 99%) arsenic trioxide and one for low-grade (minimum 95%) arsenic trioxide. There is a spread of US$ 176 to 265 per metric ton between the prices of the two grades (Loebenstein, 1992). Also, a Chinese company, SKS Mining bureau gives on internet prices for arsenic (>99%) at about US$1,325/mt and As-Cu alloy (10, 20, 30 %As) at about US$3,855/mt (SKS, 1998).

Table 2.8. Average arsenic prices (dollars per metric ton)

	1993	**1994**	**1995**	**1996**	**1997**
Trioxide, Mexican	728	706	728	728	683

Figure 2.15 shows arsenic metal price in the last years (Loebenstein, 1992; USGS, 1999). During the early 1970's, it was increasing because of the growing demand from the lead-acid batteries industry. In the mid-1970's, the price stabilized, however, during the late 1970's the United States and other countries adopted regulations related to arsenic exposure and emissions. The arsenic metal price peaked in 1980 as world producers raised their prices partly to compensate for the cost of modernizing their plants or the elimination of some capacity by producers unable to modernize their plants, principally in the United States (Loebenstein, 1994). After 1980, induced by an ample supply and a static or possibly declining demand, the arsenic metal price began a long decline.



Note:
1970-74, London prices for 99.5%-pure metal
1975-86, U.S. producer prices for 99%- to 99.5%-pure metal
1987-88, Not available
1989-91, arsenic metal prices imported from China, U.S. Bureau of Mines
1990: disruption in supply of arsenic metal from China caused a temporarily price raise
1992-98, London prices for minimum 99%-pure metal

Figure 2.15. Average arsenic metal price in the last years

2.7.2 Consumption

The United States is probably the major consumer of arsenic. In 1985, ASARCO, the sole producer closed its smelter in Tacoma, WA., resulting in the United States becoming completely dependent upon foreign suppliers. This dependency is anticipated to continue. Others consumers of arsenic are Malaysia, and the United Kingdom. Malaysia uses arsenic-based herbicides in its rubber plantations; the United Kingdom imports As_2O_3 and exports arsenic-containing pesticides and wood preservatives (Grossman, et al., 1997).

In 1990, the United States imported over 7.7 ton of arsenic metal and 28,000 ton of arsenic trioxide, well over half of world demand. In 1998 all arsenic metal and compounds consumed in the United States were imported, principally from China. It is estimated that domestic arsenic consumption ranged between 20,000 and 40,000 tons annually. The value of arsenic metal and compounds consumed domestically was estimated at $25 million. The main import sources of arsenic in the United States (1994-97) are: arsenic metal (China, 86%; Hong Kong, 5%; Japan, 3%; and other, 6%) and arsenic trioxide (China, 50%; Chile, 22%; Mexico, 11%; and other, 17%). Arsenic metal was consumed in the manufacture of nonferrous alloys, principally lead alloys for use in lead-acid batteries. It is estimated that about 15 tons per year of high-purity arsenic (99.9999%) is used in the manufacture of semiconductor material (Reese, Jr., 1998, 1999).

2.7.3 Utilisations

The end-use distribution of arsenic in recent years in the United States has been about 87% in wood preservatives, 5% in agricultural chemical, 3% in glass manufacturing, 3% as metallic arsenic in nonferrous alloys, and 2% in other uses (Resse, Jr., 1998). Table 2.9 shows US arsenic utilisation in recent years by compound (Edelstein, 1994, 1995, 1996; Resse, Jr., 1997, 1998).

Table 2.9. Utilisation of arsenical compounds in the United States (metric tons)

	1993	1994	1995	1996	1997	1998
Arsenic trioxide	27,533	26,814	29,062	27,960	30,006	38,628
Arsenic acid	-	5	(2/)	1	117	(2/)
Arsenic metal	767	1,333	557	252	909	998
Total	**28,300**	**28,152**	**29,619**	**28,213**	**31,032**	**39,626**

2/ Less than ½ unit.

Inorganic arsenical compounds of varying formulations have been used as wood preservatives in substantial quantities for over 40 years. Inorganic compounds of arsenic were once widely employed by farmers: in sheep and cattle dips as a tickicide; as dusts for killing small animals; and for controlling fungus and insects on fruit and vegetables. Today arsenical preparations are used as desiccants in cotton and in the control of weeds, grasses, prickly pear and burrs. Arsenic compounds are also used to control rodents, in insecticidal baits, and in termite treatment (Household, 1997).

Metallic arsenic is used in copper- and lead-based alloys and in electronic applications. The principal use is as a minor additive (about 0.001% to 0.5%) to lead for use in acid storage batteries to improve the strength of the lead posts and grids. Arsenic-containing lead alloys are also used in ammunition. In copper alloys, about 0.5% arsenic improves corrosion resistance and tensile strength. Arsenical copper is used in industrial plant piping, auto radiators, and admiralty brass.

Arsenic trioxide is the source for 97% of all arsenic products. In 1998, the largest end use for arsenic trioxide was in the production of wood preservatives. The three principal producers of arsenical wood preservatives were in USA: Hickson Corp., Smyrna, GA; Chemical Specialties Inc., Harrisburg, NC; and Osmose Wood Preserving, Inc., buffalo, NY. Osmose also produces arsenic acid that is used by the glass industry as a fining agent to disperse air bubbles. Arsenic was used in some herbicides for weed control. ISK Bioscience, Mentor, OH, produced the arsenical herbicide monosodium methanearsenate at a plant in Houston, TX (Reese Jr., 1999).

Chromated copper arsenate (CCA), is a waterborne preservative that is applied as water solution when cleanliness and paintability of the treated wood are required. Arsenic trioxide reacts with oxidizing agents, such as HNO_3, O_2, or H_2O_2, to form arsenic acid. The arsenic acid is then reacted with copper oxide, chromium trioxide, and water to produce a 50% CCA solution or a 72% paste (Leach, 1999). There are three types of chromated copper arsenate (CCA) approved by the AWPA (American Wood Preservers Institute) (Table 2.10). CCA type A provides excellent protection against decay fungi and termites, but is only being used by a few treaters in California. CCA type B has been commercially used in Sweden since 1950. It was included in stake tests in the United States in 1949 and has been providing excellent protection. CCA type C is by far the most common formulation of CCA being used because it has the best leach resistance and field efficacy of the three CCA formulations. CCA type C composition was selected by AWPA to encourage a single standard for CCA preservatives. Commercial preservatives of similar composition have been tested and used in United Kingdom since 1954, then in Australia, New Zealand, Malaysia, and in various countries of Africa and Central Europe; they are performing very well (Ibach, 1999).

Table 2.10. Composition of the three types of chromated copper arsenate (Ibach, 1999)

	Chromated copper arsenate		
Component	Type A	Type B	Type C
Chromium trioxide	65.5	35.3	47.5
Copper oxide	18.1	19.6	18.5
Arsenic pentoxide	16.4	45.1	34.0

In the U.K. preservatives are usually prepared from sodium dichromate, copper sulfate, and arsenic pentoxide using a similar balance of copper:chromium:arsenic as listed above for AWPA type C (Anderson, et al., 1991).

High retention levels (40 kg/m^3) of the three types of CCA preservative will provide good resistance to *Limnoria* and *Teredo* marine borer attack. In general, Douglas-fir heartwood is very resistant to treatment with CCA. Also, CCA must be used at low treating temperatures (38°C to 66°C) because they are unstable at higher temperatures (AWPI, 1999).

For satisfactory treatment and good performance, the wood must sound and be suitably conditioned. Peeling round or slabbed products is necessary to enable the wood to dry quickly enough to avoid decay and insect damage and to permit the preservative to penetrate satisfactorily. Kiln drying or air drying are used to obtain a wood with a moisture content of 19% or less. Wood that is resistant to penetration by preservatives may be incised before treatment to permit deeper and more uniform penetration. To incise, lumber and timber are passed through rollers equipped with teeth that sink into the wood to a predetermined depth, usually 13 to 19 mm.

The application of preservatives is realized by a pressure process. The conditioned wood, on cars or trams, is run into an autoclave (Figure 2.16), which is then closed and filled with a 1-2% CCA treating solution. Pressure to about 896.3 kPa forces the preservative into the wood for between 15 minutes and several hours, depending on the species of wood being treated (Leach, 1999). The AWPA specifications require that the temperature of CCA preservative during the entire pressure period not exceed the maximum of 49°C (Ibach, 1999).

Finally, the treated wood is either air dried or kiln dried, at which time the preservative undergoes fixation. During the fixation process, the copper, chrome, and arsenic react with the wood to form highly insoluble compounds. Much work has been done to determine the permanence of copper, chromium and arsenic when applied from various CCA formulations under conditions of leaching with water (Anderson, et al., 1991) (Leach, 1999). These works show that this fixation process occurs by ion exchange, absorption, and precipitation reactions and is dependent of time, temperature and pH. These studies have shown that formulations of the following composition have the greatest permanence:

Sodium dichromate $\cdot 2H_2O$	45%
Copper sulfate $\cdot 5H_2O$	35%
Arsenic pentoxide $\cdot 2H_2O$	20%

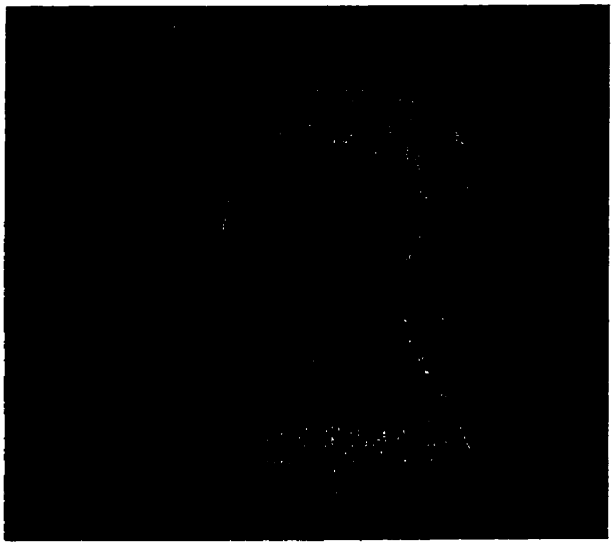


Figure 2.16. Interior view of treating autoclave at wood-preserving plant

Ammoniacal copper zinc arsenide (ACZA) and **fluor chrome arsenate phenol (FCAP)** are two other less widely used arsenical wood preservatives. Use of FCAP, among the earliest of the arsenical wood preservatives, has largely been phased out in favour of the other, more water-leach-resistant, arsenical preservatives. ACZA is used in the United States for the treatment of Douglas-fir. ACZA should contain approximately 50% copper oxide, 25% zinc oxide, and 25% arsenic pentoxide dissolved in a solution of ammonia. To aid in solution, ammonium bicarbonate is added (at least equal to 0.92 times the weight of copper oxide). A similar formulation, ammoniacal copper arsenate (ACA) is used in Canada. This preservative is used most commonly to treat refractory species, such as Douglas-fir. ACZA replaced ACA in the United States because ACZA has less arsenic and is less expensive than ACA (Ibach, 1999).

The major use of arsenical chemicals in agriculture is in cotton plantation, where they are used as herbicides and plant desiccants and defoliants. The **arsenical herbicides monosodium methanearsonate (MSMA)** and **disodium methanearsonate (DSMA)** are produced from arsenic trioxide and are used primarily in the control of grassy and broadleaf weeds in cotton production and in noncrop areas such as railroad right-of-ways. Remaining uses for arsenical pesticides include the use of sodium arsenide to combat grape measles, and lead arsenate to control grapefruit acidity.

Calcium arsenate is used as an insecticide on cotton and against certain soil insects, as a herbicide for treating turf and lawns to control weeds, and as a pesticide on fruits and vegetables. **Sodium arsenate** is used in ant killers and in animal dips as an insecticide. **Sodium arsenite** is used in low percentages in herbicides for ant control and weed control, for destroying trees and stumps, in animal dips, in pesticide baits, and for soil treatment against termites. Although there is no present commercial use for **calcium arsenite** (1:1), it was formerly used as an insecticide, pesticide, and molluscicide. **Lead arsenate** was originally a part of insecticide formulations, though this use is currently negligible.

Arsenic metal, arsenic trioxide, lead arsenate, and potassium arsenite are used in various medicines, mostly veterinary. Formerly, **disodium hydrogen arsenate** was also used in this capacity. **Potassium arsenite** as Fowler's solution is a hematinic used as a temporary medication for the treatment of myelogenous leukemia and certain skin lesions. The use of Fowler's solution as a veterinary medicine is not generally acceptable for widespread use.

Arsenic pentoxide, and arsenic trioxide are used in the manufacture of low-melting glasses. High-purity arsenic metal is used in the electronics industry for semiconductor materials. There is no present commercial use for potassium arsenate, although it has been used in fly baits, hide preservation, and textile printing and as a lab reagent.

Recently much attention is paid to the properties of gallium arsenide (GaAs) which is a semiconductor material similar to silicon with certain unique properties, such as high frequency operation for microwave circuits and optical properties for fiber optic applications (ANADIGICS, 1998). Gallium arsenide is used in manufacturing optoelectronic devices (laser diodes, light-emitting diodes (LED), photodetectors, and solar cells) and analog integrated circuits. The growing use of cellular telephone technology has resulted to a boom for GaAs demand (GaAsNet, 1999). Many GaAs manufacturers continue to introduce new devices for this market and expand capacity to meet the growing demand, mainly in the United States where in 1997, 22.4 tons of gallium in the form of GaAs were consumed (Kramer, 1998).

2.7.3.1 Arsenic Trioxide for the Treatment of Acute Promyelocytic Leukemia (APL)

Arsenicals have been used in the past for the treatment of a variety of medical conditions including syphilis. However, with the advent of modern antibiotics and chemotherapy, they fell into disfavor (Kartanjian and Koller, 1996). The outcome of APL has been altered dramatically with the addition of all-trans retinoic acid (ATRA) to anthracyclines-based chemotherapy. The activity of ATRA in APL was first reported by Chinese investigators, and confirmed in Europe and USA. Cure rates in APL have increased from 30% to above 50%. More recently, Chinese investigators have reported a major activity of arsenic trioxide (As_2O_3) in APL: 14 of 15 patients with relapsed APL achieved CR (CR rate > 90%).

Arsenic trioxide is now available for the treatment of patients with APL who have failed both chemotherapy and ATRA. Eligibility criteria require patients to have failed standard APL therapy (chemotherapy, ATRA), good performance status, and adequate organ functions. There is no age restriction and pediatric patients are eligible. Patients will receive arsenic trioxide intravenously over 2 hours daily until CR or for a maximum of 30 days. A second treatment course in CR, after a 3-6 week rest period, will be given for 5 days every week for 35 days (25 treatment days). Understanding of the effects of arsenic trioxide may guide the clinical use of arsenic compounds and provide insights into the management of leukemias that do not respond to retinoic acid.

2.7.3.2 Termite Control

Arsenic trioxide dust was the most widely used method of termite control until the organochlorines became available approximately forty years ago (Household, 1997). Mixed with ferrous oxide, it is still used to destroy the colony nest, but can be applied only by a licensed pest control operator with a permit. Treatment is only effective for certain species of termites and does not provide long-term protection. It is only a form of control for active infestations and does not prevent future colonies.

Arsenic trioxide application should be undertaken as part of a long-term integrated termite management strategy, and treatment should not be applied in situations where it is considered it will be ineffective, as in fencing or stored firewood timbers; and should not be used for direct nest destruction in trees, as it may result in the death of the tree. The less toxic chemical, Permethrin, is preferable.

2.8 Ambient Standards and Guidelines

Ambient standards and guidelines for arsenic are aimed at protecting the population, livestock and other organisms from the exposure to ambient arsenic. Table 2.11 presents reference standards and guidelines for ambient levels of arsenic in water for the European Union, the United States, Canada and the World Health Organization (Health Canada, 1992; World Bank, 1998). In order to protect health, acceptable arsenic concentrations in ambient water focus on water intended for drinking. Table 2.12 presents the permissible exposure limit at work of arsenic in air in the some countries (Grossman, et al., 1997).

Table 2.11. Reference standards and guidelines for ambient levels of arsenic in water

Value, µg/L	EU, limit	EU, guide	US EPA standard	Canada IMAC[3]	WHO, guide
Drinking water	50		50	25	10
Surface water intended for drinking	50[1] 100[2]	10[1] 50[2]			

[1] Before normal treatment, [2] Before intensive treatment

[3] IMAC: Interim maximum acceptable concentration for arsenic in drinking water

Table 2.12. Permissible exposure limit at work of arsenic in air

Air (mg/Nm^3)	U.S.	Germany	Japan	Sweden
Calcium Arsenate	1.0	0.2		
Arsine	0.2	0.05 ppm	0.2	0.05
All other inorganic compounds	0.01	0.2	0.5 (As_2O_3)	
Organic compounds (as As)	0.5	1.0		
Observations			Maximum allowable workplace air concentration	All arsenic compounds

2.8.1 Regulations for Arsenic Effluents in the Metallurgical Industry

Due to the toxicity of arsenic and its compounds, environmental regulators have set very low levels for arsenic in aqueous effluents for the metallurgical industry (Table 2.13).

Table 2.13. Environmental legislation for arsenic effluents in the metallurgical industry

	Aqueous effluents, mg/L	Reference
The United States	1.0	Piret, 1999
Germany	0.5	Piret, 1999
Canada	0.5[1]	Environment Canada, 1977
Québec	0.5[1]	Ministère de l'Environnement, 1989
Japan	0.1	Environment Agency of Japan, 1999

[1] Monthly arithmetic mean concentration

2.8.1.1 The Clean Air Act in the United States

In 1990 the Congress amended the Clean Air Act and the Environmental Protection Agency (EPA) was required to develop technology-based emissions standards for stationary sources of the 188 hazardous air pollutants (e.g., arsenic compounds) (US EPA, 1990). EPA published a list of industrial source categories that emit one or more of these hazardous air pollutants and listed categories of "major" sources ("major source" means any stationary source or group of stationary sources located within a contiguous area and under common control that emits or has the potential to emit considering controls, in the aggregate, 10 tons per year or more of any hazardous air pollutant or 25 tons per year or more of any combination of hazardous air pollutants) and issue Maximum Achievable Control Standards (MACT) for each category over a specified timetable. Emissions of 188 toxic pollutants, typically carcinogens, mutagens, and reproductive toxins, must be reduced within 10 years. Companies that initiate partial controls before the deadlines set for MACT (Maximum Achievable Control Technology) can receive extensions (US EPA Journal, 1991).

Today, EPA is proposing regulation which would reduce emissions of eleven hazardous air pollutants (compounds containing antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium) from the seven primary copper smelters operating in the United States. EPA's proposed rule would reduce emissions of hazardous metal compounds from 190 metric tons per year to 155 metric tons per year, an 18 percent reduction. This represents approximately 6 metric tons per year of arsenic and 22 metric tons per year of lead. In reducing emissions of toxic metal compounds and in turn associated exposure levels, EPA's proposed action would also reduce occupational exposures. This action is consistent with the Pollution Prevention Act of 1990 (US EPA, 1998c).

2.8.1.2 The Accelerated Reduction and Elimination of Toxic (ARET) Program in Canada

ARET is a Canadian industry/government voluntary emission reduction program that targets 117 toxic substances (Environment Canada, 1992). In total, 303 facilities from 162 companies and government organizations are participating. The ARET goal is to achieve a 90% reduction of persistent, bioaccumulative and toxic (PBT) substances emissions and a 50% emission reduction of other 87 toxic substances by the year 2000. Since the base year (1992), emissions by ARET participants have been decreased by 100,000 tons of toxic substances (Environment Canada, 1999).

Emissions from the mining and smelting sector in 1997 amounted to 2,309 tons (17% of total ARET emissions). From base-year levels of 7,854 tons, emissions have been reduced by 5,545 tons or 71% as of 1997. Inorganic arsenic emissions in this sector amounted to 116 tons in 1997, down by 32 tons from the previous year. From base-year levels of 341 tons, total ARET arsenic emissions have been reduced by 53% and it is expected reduction of 80% in the year 2000 (Environment Canada, 1999).

2.8.2 World Bank Emission Guidelines

Emissions levels for the design and operation of each project must be established through the Environmental Assessment (EA) process, based on country legislation and the *Pollution Prevention and Abatement Handbook* as applied to local conditions (World Bank, 1998). The emission levels selected must be justified in the EA and acceptable to the World Bank Group. The following guidelines present emission levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance; any deviations from these levels must be described in the World Bank group project documentation. All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours. For copper smelters air emissions levels shown in Table 2.14 should be achieved. The environmental assessment should address the build-up of heavy metals from particulate fall-out in the vicinity of the plant over its projected life. For copper smelters, the effluent emission levels shown in Table 2.15 should be achieved.

Table 2.14. Emissions from copper smelting

Parameter	Maximum value, mg/Nm^3
SO_2	1,000
Arsenic	0.5
Cadmium	0.05
Copper	1
Lead	0.2
Mercury	0.05
Particulate matter– smelter	20
Particulate matter – other sources	50

Table 2.15. Effluents from copper smelting

Parameter	Maximum value, mg/L
PH	6-9
Total suspended solids	50
Arsenic	0.1
Cadmium	0.1
Copper	0.5
Iron	3.5
Lead	0.1
Mercury (total)	0.01
Zinc	1.0
Total metals	10
Temperature increase	less than or equal to 3°C[1]

[1] The effluent should result in a temperature increase of no more than 3 degrees Celsius at the edge of the zone where initial mixing and dilution take place. Where the zone is not defined, use 100 meters from the point of discharge.

2.9 Arsenic Removal from Drinking Water

2.9.1 Background

In water, the most common valence states of arsenic are As (V), or arsenate, which is more prevalent in aerobic surface waters and As (III), or arsenite, which is more likely to occur in anaerobic ground waters (Dainichi, 1998). In the pH range of 4 to 10, the predominant As (III) compound is neutral in charge, while the As (V) species are negatively charged. Removal efficiencies for As (III) are poor compared to removal As (V) by any of the technologies evaluated due to the negative charge.

During removal of arsenic from water, As (III) must be converted to As (V) by oxidation because As (III) cannot be removed properly by the above methods. The technologies under review perform most effectively when treating arsenic in the form of As (V). Data on oxidants indicate that chlorine, hydrogen peroxide, bleaching powder, ferric chloride, and potassium permanganate are effective in oxidizing As (III) to As (V). Pre-oxidation with chlorine may create undesirable concentrations of disinfection by-products. Ozone should oxidize As (III) to As (V), but no data are available on its performance. Bleaching powder is the cheapest and most acceptable oxidizing agent.

2.9.2 Technologies

Coagulation/Filtration (C/F) is an effective treatment process for removal of As (V) according to laboratory and pilot-plant tests. The type of coagulant and dosage used affects the efficiency of the process. Within either high or low pH ranges, the efficiency of C/F is significantly reduced. Liquid aluminum sulfate (ALUM) performance is slightly lower than ferric sulfate, $Fe_2(SO_4)_3$. Other coagulants, e.g., $FeCl_3$, are also less effective than ferric sulfate. Disposal of the arsenic-contaminated coagulation sludge may be a concern.

Lime Softening (LS), in which CaO is added when operating within the optimum pH range of greater than 10.5 it is likely to provide a high percentage of As removal for influent concentrations of 50 μg/L. However, it may be difficult to reduce consistently as to 1 μg/L by LS alone. Systems using LS may require secondary treatment to meet that goal.

Activated Alumina (AA), in which Al_2O_3 is used, is effective in treating water with high total dissolved solids (TDS). However, selenium, fluoride, chloride, and sulfate, if present at high levels, may compete for adsorption sites. AA is highly selective towards As (V); and this strong attraction results in regeneration problems, possibly resulting in 5 to 10 percent loss of adsorptive capacity for each run. Application of point-of-use treatment devices would need to consider regeneration and replacement.

Ion Exchange (IE), where different types of resin are used, can effectively remove arsenic. However, sulfate, TDS, selenium, fluoride, and nitrate compete with arsenic and can affect run length. Passage through a series of columns could improve removal and decrease regeneration frequency. Suspended solids and precipitated iron can cause clogging of the IE bed. Systems containing high levels of these constituents may require pre-treatment.

Reverse Osmosis (RO) provides removal efficiencies of greater than 95% at operating pressure. The water recovery is the volume of water produced by the process divided by the influent stream (product water/influent stream). Discharge of reject water or brine may also be a concern. The increased water recovery can lead to increased costs for arsenic removal.

Electrodialysis Reversal (EDR) is expected to achieve removal efficiencies of 80%. One study demonstrated arsenic removal to 3 μg/L from an influent concentration of 21 μg/L.

2.9.3 Prospective Technologies

Ion Exchange with Brine Recycle. Research recently completed by the University of Houston (Clifford) at McFarland, CA and Albuquerque, has shown that ion exchange treatment can reduce arsenic (V) levels to below 2 μg/L even with sulfate levels as high as 200 mg/L. Sulfate does impact run length, however; the higher the sulfate concentration, the shorter the run length to arsenic breakthrough. The research also showed that the brine regeneration solution could be reused as many as 20 times with no impact on arsenic removal provided that some salt was added to the solution to provide adequate chloride levels for regeneration. Brine recycle reduces the amount of waste for disposal and the cost of operation.

Conventional Iron/Manganese (Fe/Mn) Removal Processes. Iron coagulation/filtration and iron addition with direct filtration methods is effective for arsenic (V) removal. Source waters containing naturally occurring iron and/or manganese and arsenic can be treated for arsenic removal by using conventional Fe/Mn removal processes. These processes can significantly reduce the arsenic by removing the iron and manganese from the source water based upon the same mechanisms that occur with the iron addition methods. The addition of iron may be required if the concentration of naturally occurring iron/manganese is not sufficient to achieve the required arsenic removal level.

2.9.4 Arsenic Disposal from Drinking Water Waste

Disposal of the arsenic-contaminated coagulation sludge from the Coagulation/Filtration and Lime Softening technologies may be a concern. For large treatment plant, a large body of water would likely be needed to discharge the contaminated brine stream from the Reverse Osmosis/Nano-Filtration technologies. Inland treatment plants would possibly need either some pre-treatment prior to discharge or would need to discharge to the sanitary sewer due to the increase in salinity. Discharge to sanitary sewers may require pre-treatment to remove high arsenic levels. The waste stream produced by Ion Exchange (IE)/Activated Alumina (AA) technologies is a highly concentrated brine with high Total Dissolved Solid. These brine streams may required some pre-treatment prior to discharge to either a receiving body of water or the sanitary sewer. The Table 2.16 shows a summary of the advantages and disadvantages of available technologies for arsenic treatment (Dainichi, 1998).

Table 2.16. Available technologies for arsenic removal from drinking water

Method	Advantages	Disadvantages
Co-precipitation:	No monitoring of a break through is required. Relatively low cost simple chemicals. Low capital cost.	Serious short and long term problems with toxic sludge. Multiple chemicals required Operation requires training and discipline.
Alum coagulation	Durable powder chemicals normally available.	Efficient pre-oxidation is a must.
Iron coagulation	More efficient than alum on weigh basis.	Medium removal of As (III)
Lime softening	Most common chemicals.	Re-adjustment of pH is required.
Sorption techniques:	No daily sludge problem	Requires monitoring of break through or filter use. Requires periodical regeneration or medium shift.
Activated alumina	Relatively well known and commercially available	Re-adjustment of pH is required.
Iron coated sand	Expected to be cheap No regeneration is required	Yet to be standardized. Toxic solid waste
Ion exchange resin	Well defined medium and hence capacity.	High cost medium High tech operation & maintenance Regeneration creates a sludge problem
Other Sorbents	Plenty of possibilities & combinations	Not yet property studied
Membrane techniques:	Well defined performance High removal efficiency No solid waste Low space requirement Capable of removing other contaminants, if any	High running costs. High investment costs. High tech operation and maintenance Toxic wastewater Re-adjustment of water quality is required.
Reverse Osmosis		Membrane does not withstand oxidizing agents.
Electrodialysis		Membrane does not withstand oxidizing agents.

CHAPTER III

ARSENIC DISTRIBUTION IN COPPER SMELTERS

Arsenic is a common impurity in various feedstocks treated pyrometallurgically. Typical examples are: auriferous refractory arsenical pyrites, copper, zinc, nickel, cobalt and lead sulfide concentrates. Copper sulfide concentrates; frequently contain the minerals arsenopyrite (FeAsS), enargite (Cu_3AsS_4), realgar (As_2S_3), orpiment (As_4S_4), and tennantite $(Cu,Fe)_{12}As_4S_{13}$. Historically arsenic has either been avoided in the mining operation or eliminated in the smelter. These concepts have been managed to result in acceptable arsenic content in the input to the copper refinery. During the smelting-converting process for copper, most of the arsenic is volatilised and reports in the flue dusts as a sulfide (As_2S_3) or oxide (As_2O_3) while a minor fraction goes to the slag, matte, and blister copper.

3.1 Factors Affecting the Distribution

For a given level of arsenic input to a copper smelter the amount in copper anode will be a function of the process. The variables having a pronounced effect on these unit distributions are matte grade and off-gas temperature. Other variables such as mineralogy, bath temperature, oxygen partial pressure, presence of other impurities, etc., have minor effects (Cocquerel and Shaw, 1983).

3.1.1 Behavior in Roasting

To obtain a matte of a desired composition suitable for further processing, it is sometimes required to eliminate a certain amount of sulfur and volatile impurities (e.g., arsenic) present in the concentrate before melting. This is normally done by partial oxidation in a multiple hearth, e.g. at El Indio mine (Smith, 1986), or a fluidized bed furnace, e.g. at Lepanto smelter (Piret and Melin, 1989). Roasting has been the subject of considerable research (Weisenberg, et al., 1979; Landsberg, et al., 1980; Lindkvist and Holmström, 1983; Vircikova and Palfy, 1998). Arsenic removal by volatilization depends upon temperature, residence time, and the type of atmosphere in the roasting unit. It can be readily achieved if oxidation of the sulfide is conducted in a limited supply of air. Under such conditions arsenic trioxide, As_2O_3, is formed which sublimes already at 218°C and can be separated from the gas stream in the filtration units (Habashi, 1986):

$$As_2S_3 + 4\tfrac{1}{2}O_2 \rightarrow As_2O_3 + 3SO_2 \qquad (3.1)$$

In the presence of excess air, however, arsenic oxide, As_2O_5, is formed which is nonvolatile and melts at 315°C:

$$As_2S_3 + 5\tfrac{1}{2}O_2 \rightarrow As_2O_5 + 3SO_2 \qquad (3.2)$$

Usually this oxide combines with any ferric oxide in the ore to form ferric arsenate:

$$Fe_2O_3 + As_2O_5 \rightarrow 2FeAsO_4 \qquad (3.3)$$

As a result, arsenical pyrite is usually oxidized in a limited supply of air to volatilize As_2O_3. Under these conditions, magnetite will be the major iron oxide in the cinder:

$$3FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2 \qquad (3.4)$$

3.1.2 Behavior in Smelting

The purpose of the smelting process is to separate the metal sulfides in the concentrate or calcine from the gangue, and this is achieved by smelting in presence of fluxes at about 1250°C. During smelting the raw materials fed into the furnace separate into two liquid layersa slag layer containing the gangue and fluxing materials and beneath it a matte consisting of metallic sulfides.

Arsenic will be partially eliminated due to the formation of a volatile oxide. Being formed at high temperatures, a matte will be composed of the most stable sulfides. For example Cu_2S, FeS are the most stable sulfides of copper and iron, respectively; they are also the major components of mattes.

Persson, et al. (1986) reported that arsenic removal reverses when matte approaches 80% Cu. This is thought to be due to (i) the presence of metallic copper in these very high grade mattes and (ii) the high solubility of arsenic in metallic copper (Biswas and Davenport, 1994). Five different schemes for various combinations of pyrometallurgical processes are shown in Figures 3.1 to 3.5: Reverberatory + converting, Teniente + converting, Noranda + converting, flash smelting + converting and Mitsubishi smelting and converting. The arsenic balance from the references indicated are shown. Table 3.1 and Figure 3.6 summarise arsenic distribution and elimination during smelting and converting of the five smelting systems shown.

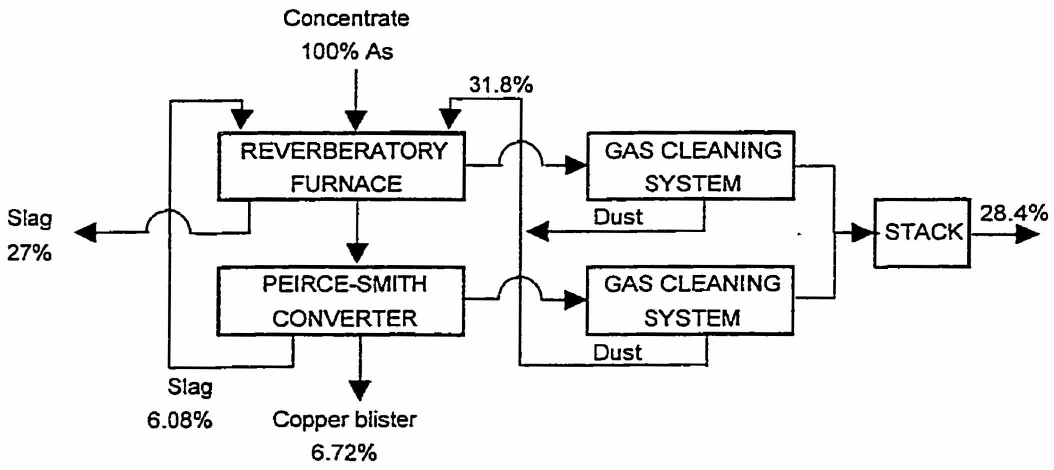


Figure 3.1. Reverberatory furnace and Peirce-Smith converter (Vircikova and Imriš, 1995; Wiertz and Rozas, 1996).

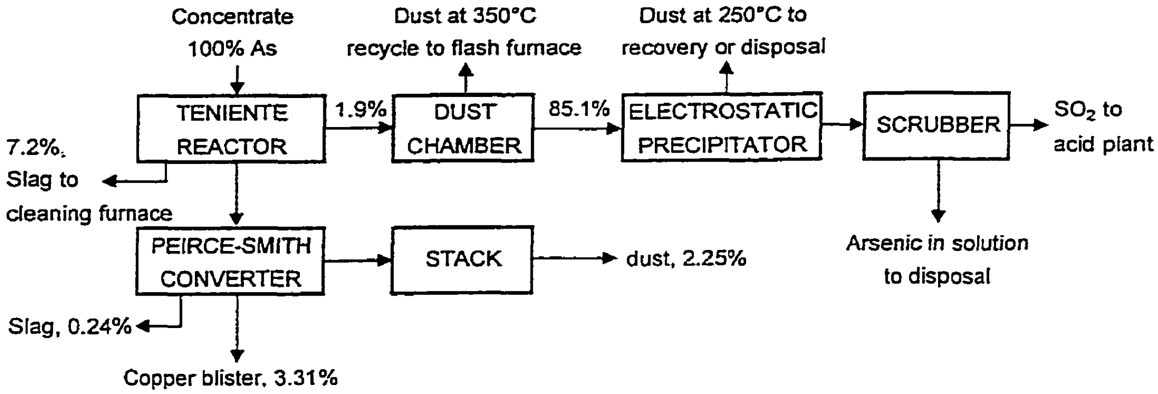


Figure 3.2. Teniente reactor (71.1% Cu white metal) and Peirce-Smith converter (Mendoza and Luraschi, 1993; Mendoza, et al., 1995).

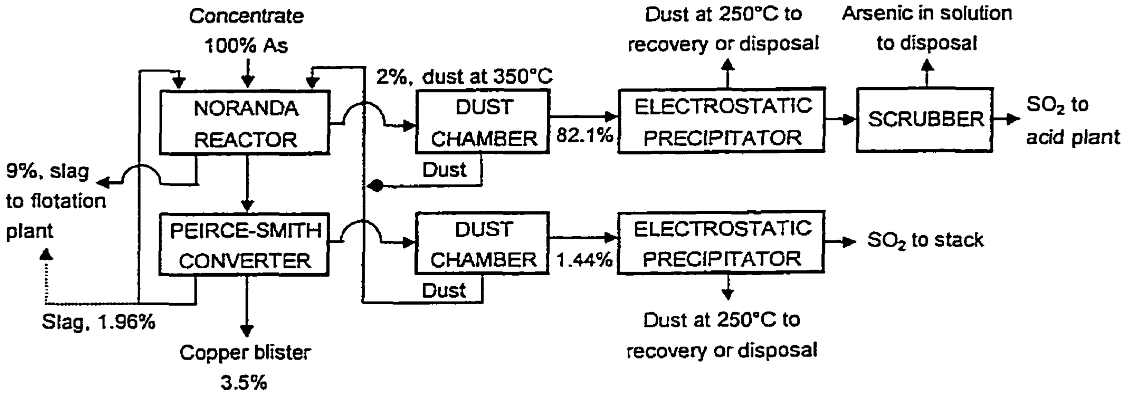


Figure 3.3. Noranda reactor (70% Cu matte) and Peirce-Smith converter (Mackey, et al., 1979; Persson, et al., 1986)

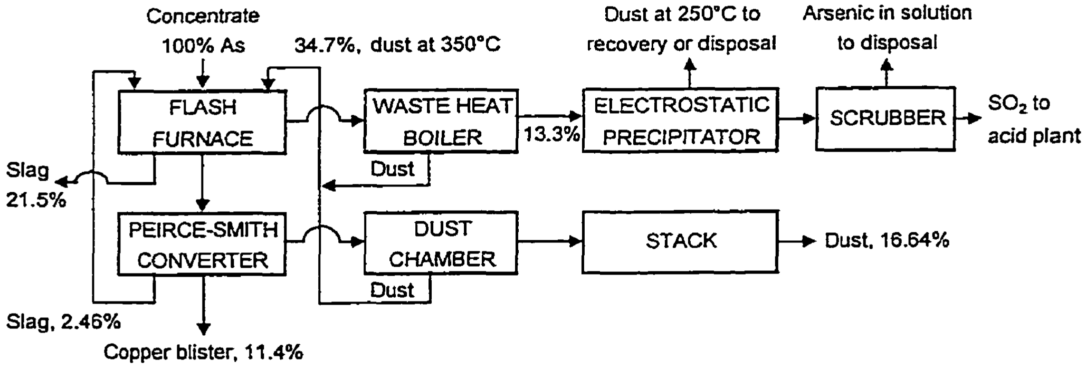


Figure 3.4. Outokumpu flash furnace (60% Cu matte) and Peirce-Smith converter (Mendoza, et al., 1995; Zeping, 1999).

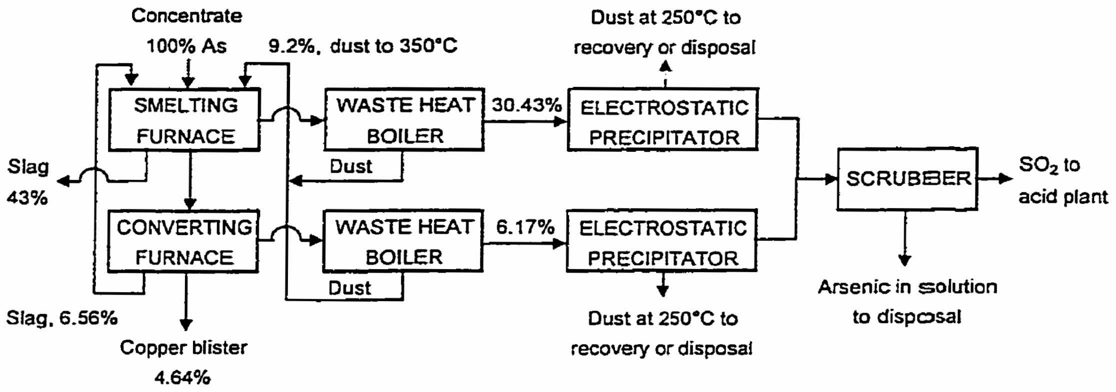


Figure 3.5. Mitsubishi smelting (69% Cu matte) and converting furnace (Chenier, et al.,1992).

Table 3.1. Arsenic distribution in different pyrometallurgical processes (%)

Distribution with respect to imput	Reverberatory furnace + PSC	Teniente reactor + PSC	Noranda reactor + PSC	Outokumpu furnace + PSC	Mitsubishi furnace
Blister	6.7	3.3	3.5	11.4	4.6
Slag from furnace	27.0	7.2	9.0	21.5	43.0
Slag from PSC	6.1	0.2	2.0	2.5	6.6
Dust collected at 350°C	31.8	1.9	2.0	34.7	9.2
Dust at 250°C	-	85.1	83.5	13.3	36.6
Dust to stack	28.4	2.3	-	16.6	-
Total	100.0	100.0	100.0	100.0	100.0

PSC: Peirce-Smith converter

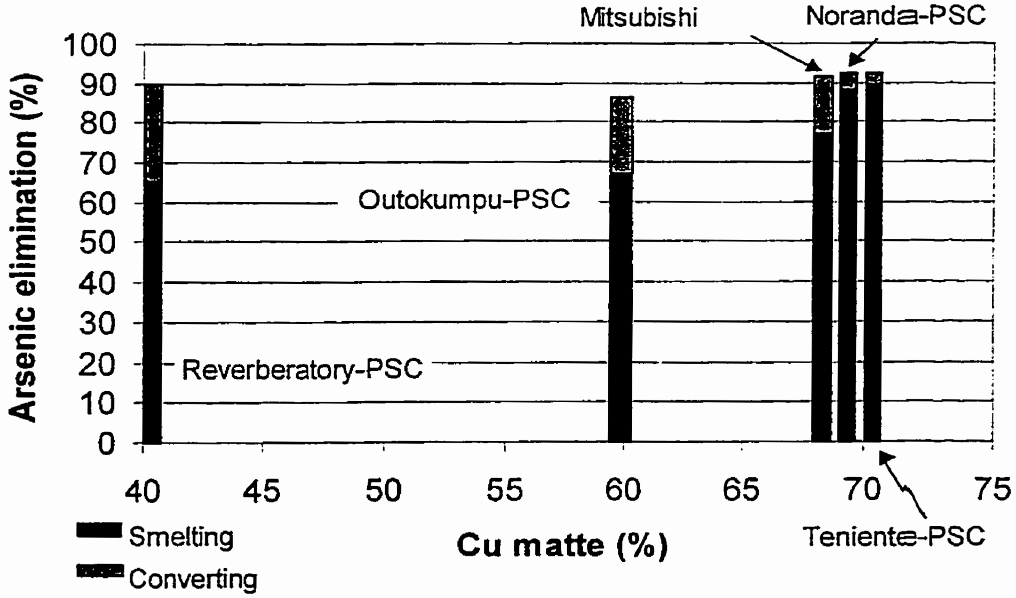


Figure 3.6. Arsenic elimination during smelting and converting in different processes

The differences of arsenic elimination processes (smelting/converting) can be explained by the variations in operating conditions at the various smelters, such as feed composition, smelting temperature, converting rate, oxygen enrichment, gas composition, the analysis and relative quantities of products, etc. Arsenic elimination, occurs principally during the smelting stage by volatilization and slagging:

- In reverberatory furnace, arsenic elimination occurs by volatilization because the atmosphere is slightly reducing, and by slagging because of the large volume of the furnace. In Peirce-Smith converter, more arsenic is eliminated by volatilization and by slagging.

- In Teniente and Noranda reactors, arsenic elimination by volatilization is high and by slagging is low. Arsenic elimination in the Peirce-Smith converter increases with the extent of air blowing, thus it is high when low matte grades are treated (Mackey, et al., 1979; Mendoza and Luraschi, 1993). Arsenic elimination in these operations is similar. Both are operating at the same matte grade, about 70% Cu. The oxygen enrichment for the Teniente and Noranda reactor is 38 and 33% O_2, respectively, while the Peirce-Smith converters operate with unenriched air.

- In Outokumpu flash furnace and Peirce-Smith converter less arsenic is eliminated by volatilization because the atmosphere is strongly oxidizing and this favors the formation of As_2O_5 thus more arsenic is eliminated in the slag. It can be seen that the arsenic elimination is less than in the Teniente and Noranda operations due to the recycling of large amounts of dust.

- In the Mitsubishi smelting, a significant fraction of arsenic reports to both the slag and dusts. In converting furnace, arsenic is split into approximately the same proportions among slag, dust and blister copper. Additional arsenic removal from the blister to the slag is possible by increasing the oxidation (Chenier, et al., 1992). The oxygen enrichment for the smelting and converting operation is 48 and 33% O_2, respectively.

3.1.3 Behavior in Gas Handling System

Arsenic associated with metallurgical gases is present as the dimer As_4O_6. After cooling the gases, arsenic condensation takes place; depending on the arsenic content, condensation starts at a gas temperature of 200°C and is completed at 40-80°C (Figure 3.7). According to the diagram the concentrations of volatile arsenic at sea level are as follows:

Temperature, °C	Arsenic (as As_4O_6) mg/Nm^3
70	0.9
100	12
110	29
130	148

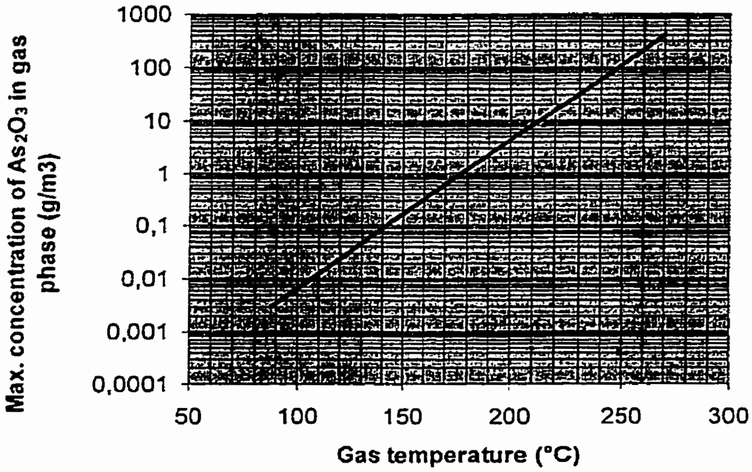


Figure 3.7. Concentration of As_2O_3-vapour as a function of temperature (Expressed in As_2O_3 per m^3 gas at 0°C and 1,013 kPa) (Piret, 1999).

In order to have sufficiently low levels of arsenic prior to entering the acid plant, gases must be cooled then submitted to a process step eliminating the bulk of arsenic as As_2O_3. Subsequent to this step, the residual arsenic is eliminated from the gas by a wet process, usually in a electrostatic precipitator. Different dry and wet methods for removal of arsenic from SO_2-bearing gases are described by Dalewski (1999).

Arsenic content in the dusts recovered in the cooling chambers and in electrostatic precipitators ranges between 3 and 30%, depending on the process conditions (arsenic content in the concentrates, type of furnace, concentrate feed system, temperature of the gases in the dust collecting equipment) and represents usually as much as 60% of the total amount of arsenic initially associated with the gas (Wiertz, et al., 1998). Recycle of dusts to the smelting furnace causes an increase of arsenic and other impurities in the circuit, ultimately increasing their concentrations in the anode copper destined for refining (Hoffman, 1993). Therefore, this practice should be ruled out. Finally, arsenic can be recovered as pure arsenic trioxide from arsenic-containing dusts or treated by hydrometallurgical methods prior to disposal as it is shown in chapter 5 and 6 of this thesis.

CHAPTER IV

ARSENIC IN THE CHILEAN COPPER INDUSTRY

4.1 Copper Production

Mining is one of the most important sectors in the Chilean economy. In 1997, it constituted 8.0% of gross domestic product (GDP) and accounted for 50% of Chilean exports. The industry comprises over two hundred companies, employing approximately 87,000 people or 1.7% of the work force. In the last years, Chile continued to be the top producer and exporter of copper, in terms of volume (Table 4.1) and value, and it was recognized by the world mining community as being the single most active mining country, in terms of new development and investment; of the total $5.04 billion in foreign investment in 1997, $1.61 billion was in mining (Velasco, 1996, 1997b).

Table 4.1. Chilean copper mine production (thousand metric tons)

	1995	1996	1997	1998	1999^e
World	10,100	11,103	11,487	12,312	12,600
Chile	2,489	3,116	3,392	3,691	4,360
% Chilean Production	**24.64**	**28.06**	**29.53**	**29.98**	**34.60**

Source: Comisión Chilena del Cobre (Cochilco, 1999), Edelstein, 1998, 2000
^{e}: *Estimated*

Regarding, the Chilean copper concentrate production, COCHILCO (1996) reported that it will have an important increase in the next years because of the startup of new copper mine projects and the increase of production in actual operations, e.g., La Candelaria, Escondida, Collahuasi, Los Pelambres, which will generate a growing concentrate availability in Chile.

The main companies producing copper concentrate in Chile are shown in Table 4.2. In the year 2000, Chile is producing more than 3 millions of tons of copper in the form of concentrate, which is 38% of total copper concentrate production of western world.

Regarding the Chilean smelting production, it has been almost kept the same in the last years (Table 4.3). However, Noranda Chile S.A. (Altonorte smelter) will increase its copper smelting capacity from 160,000 to 290,000 mt/y and its sulfuric acid production from 250,000 to 700,000 mt/y. The cost of this expansion will be US$ 170 million, which is expected to be completed in 2003 (NORANDA, 1999).

Table 4.2. Chilean copper concentrate production (Thousand metric tons)

Company	Mine	1995	1996	1997	1998	1999	2000
Codelco Chile	Chuquicamata	473	457	465	495	443	432
Codelco Chile	El Salvador	74	73	70	68	63	62
Codelco Chile	El Teniente	319	338	330	331	333	316
Codelco Chile	Andina	146	141	138	144	237	244
Minera Candelaria	Candelaria	150	140	140	172	172	172
Minera Doña Inés	Collahuasi	0	0	0	150	330	330
Minera El Indio	El Indio	35	35	40	40	40	40
Minera Disputada	Los Bronces	132	132	132	133	132	135
Minera Disputada	El Soldado	61	61	61	61	61	61
Minera Escondida	Escondida	439	720	720	720	715	715
Min. Los Pelambres	Los Pelambres	23	24	24	24	230	230
Min. Mantos Blancos	Mantos Blancos	75	46	46	46	46	46
Others		161	169	171	208	205	292
Total		**2,088**	**2,336**	**2,337**	**2,592**	**3,007**	**3,075**

Source: Comisión Chilena del Cobre (COCHILCO, 1996)

Table 4.3. Chilean copper smelting production (Thousand metric tons)

Company	Smelter	1996	1997	1998	1999	2000
Codelco Chile	Chuquicamata, Caletones, Potrerillos	913	935	964	967	953
ENAMI	Ventanas, Hernán Videla Lira (Paipote)	194	194	181	194	194
Disputada de las Condes	Chagres	92	105	105	105	105
Noranda Chile S.A.	Altonorte(1)	108	130	144	153	153
Total		**1,307**	**1,387**	**1,394**	**1,419**	**1,405**

(1)ex Refimet Smelter.

Source: Comisión Chilena del Cobre (Cochilco, 1996).

La Corporación Nacional del Cobre (CODELCO) and la Empresa Nacional de Minería (ENAMI) are state copper corporations. ENAMI operates a number of small mines and concentrators, the latter taking ore from small miners on a toll basis, but its most important function is to purchase and smelt copper concentrates at its Paipote and Ventanas Smelters. CODELCO has smelters at three of its divisions: Chuquicamata, El Salvador (Potrerillos smelter), and El Teniente (Caletones smelter) which processes not only its own concentrate and also from other mines, e.g., Andina, Escondida, Candelaria, and El Indio. At present, the main copper smelters in Chile are (Figure 4.1):

- Chuquicamata, Codelco Chile, Chuquicamata Division.
- Altonorte, Noranda Chile S.A., Antofagasta.
- Paipote, Hernán Videla Lira, ENAMI, Copiapó.
- Potrerillos, Codelco Chile, El Salvador Division, El Salvador.
- Ventanas, ENAMI, Puchuncavi, Quintero.
- Chagres, Minera Disputada de Las Condes, Exxon, Catemu Valley.
- Caletones, Codelco Chile, El Teniente Division, Rancagua.

In addition, El Indio mine belonging to Barrick Chile, has a roasting plant, which recovers arsenic trioxide from its copper concentrate.

Figure 4.1. Copper smelters in Chile

The technology utilized at the Chilean smelters is shown in Table 4.4. Schemes of Chilean smelters are shown in Figure 4.2 to 4.8.

Table 4.4. Smelting technologies in the Chilean smelters

Smelter	Technology	Smelting Capacity (t/d)	Copper production (t/y)	H_2SO_4 Production (t/d)	Sulfur Captured (%)	Reference
Chuquicamata	1 Outokumpu flash furnace	2,200	500,000	5,500	87	
	2 Teniente reactor (5 x 22 m)	1,350 each				Queirolo, 1998
	5 Peirce Smith converter					Muñoz, 1996
	1 Teniente slag cleaning furnace					
Caletones	1 Reverberatory furnace	400	355,000	1,500	37	
	2 Teniente reactor (5 x 22 m)	1,650 each		(design)		Muñoz, 1996
	4 Peirce Smith converter					Alvarado and Godoy, 1999
	3 Teniente slag cleaning furnace					
Potrerillos	1 Reverberatory furnace	550	150,000	1,877	N.A.	
	1 Teniente reactor (4 x 18 m)	950		(design)		Muñoz, 1996
	4 Peirce Smith converter					Rojas, et al., 1999
	1 Teniente slag cleaning furnace					
Ventanas	1 Teniente reactor (5 x 22 m)	1,150	115,000	900	90	González, et al., 1995
	3 Peirce Smith converter					Díaz, et al., 1997
	1 Electric furnace					
Paipote[1]	1 Teniente reactor (4 x 15 m)	850[2]	73,786[3]	706	88.2	
	2 Peirce Smith converter					Rojas, 2000
	1 Slag settling furnace					
Chagres[4]	1 Outokumpu flash furnace	1,320	123,000	1,200	95	
	3 Peirce Smith converter					Duran, 1999
	2 Teniente slag cleaning furnace					
Altonorte	1 Reverberatory furnace	1,150[5]	160,000	750	80	Mast, et al., 1999
	3 Peirce Smith converter					
Total		14,570	1,476,786	12,433	-	

N.A.: Not available

[1] Results obtained in 1999, [2] green concentrate + concentrate from slag flotation plant, [3] 73,786 = 72,762 anodes + 1,024 blister.

[4] Results obtained in 1998, [5] 70 t/d of copper cement

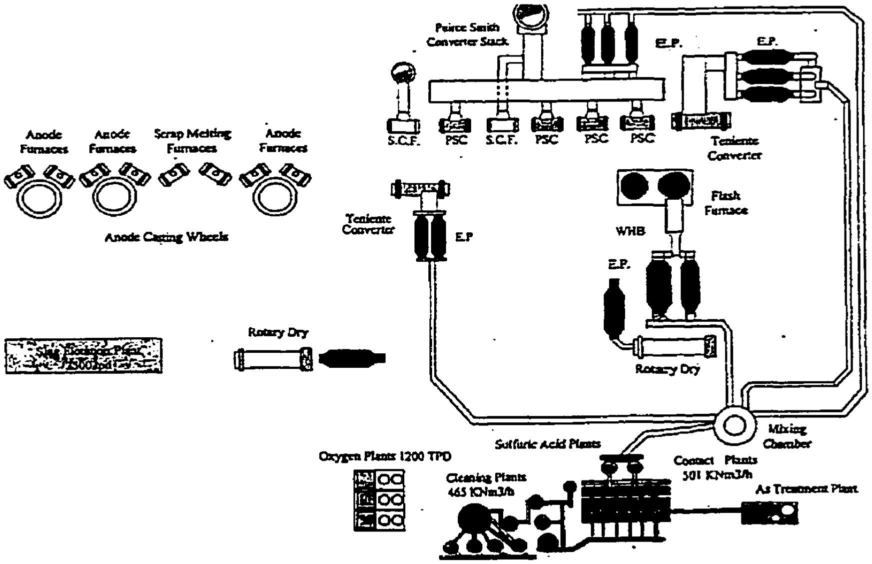


Figure 4.2. Chuquicamata smelter (after Queirolo, 1998)

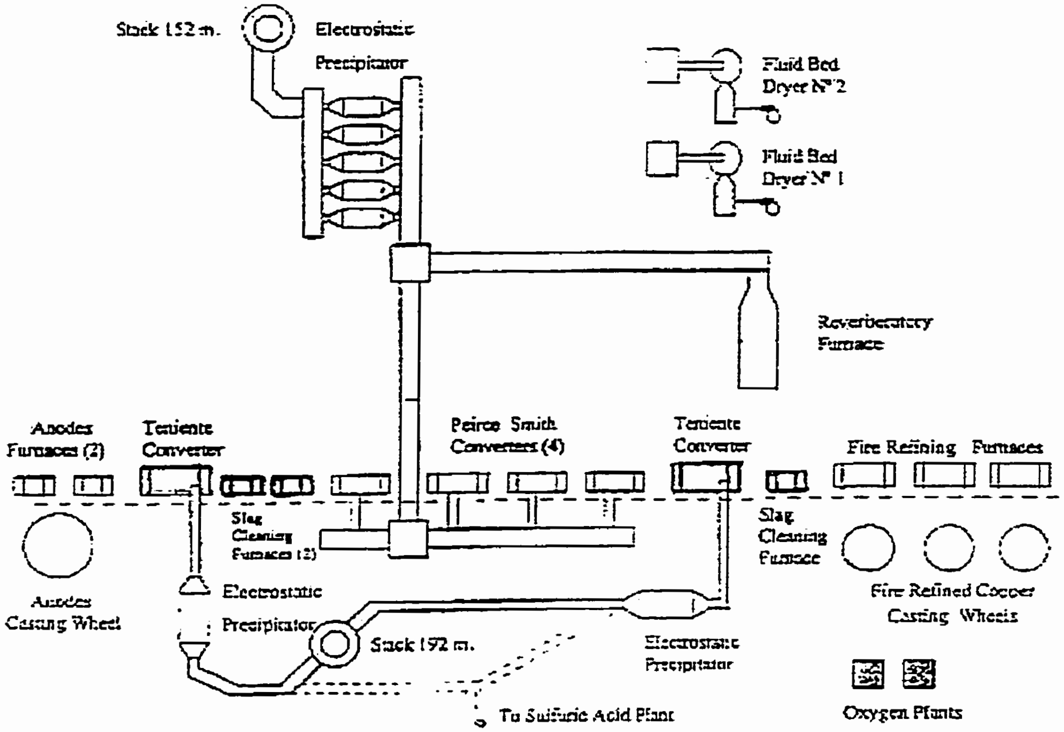


Figure 4.3. Caletones smelter (after Muñoz, 1996)

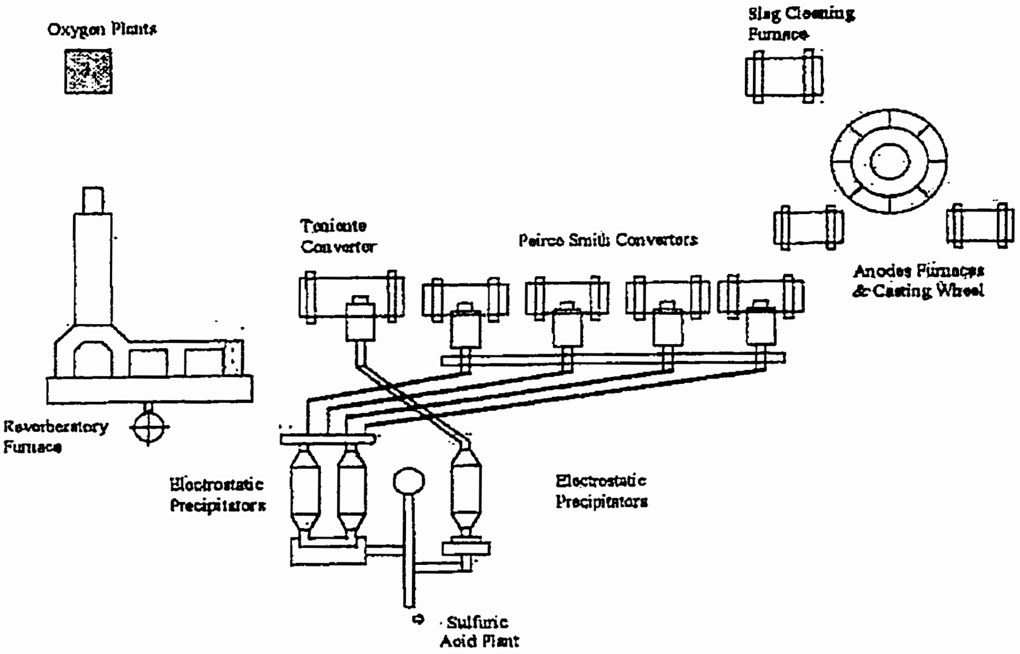


Figure 4.4. Potrerillos smelter (after Muñoz, 1996)

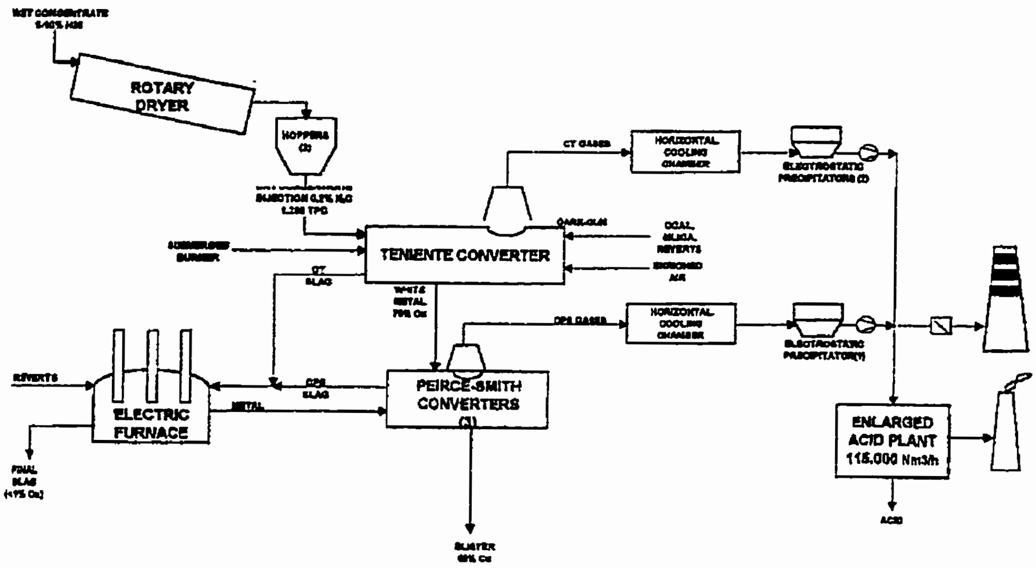


Figure 4.5. Ventanas smelter (after González, et al., 1995)

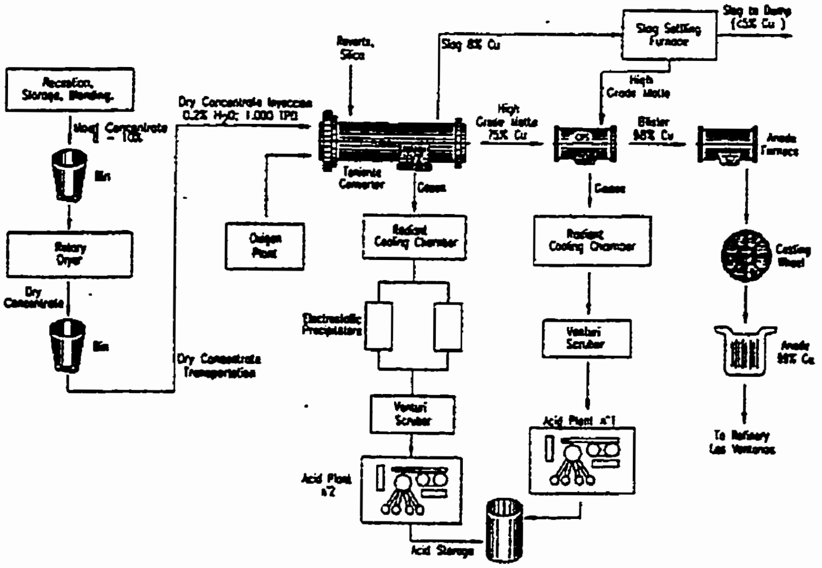


Figure 4.6. Paipote smelter (after Rojas and Sanhueza, 1999)

The slag settling furnace is an alternative slag treatment for the Teniente reactor, which permits to obtain a high grade matte, having 74-75% Cu. The final slag content is 3-4% Cu, it is cooled and sent to flotation. The concentrate is returned to melt. An electric furnace will replace this slag settling furnace to a cost of US$ 18.7 million, which is expected to be completed in 2001 (Minería Chilena, 2000).

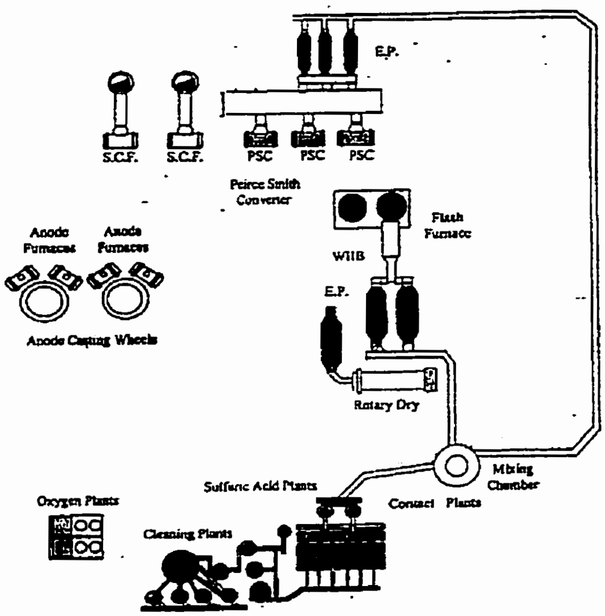


Figure 4.7. Chagres smelter (after Duran, 1999)

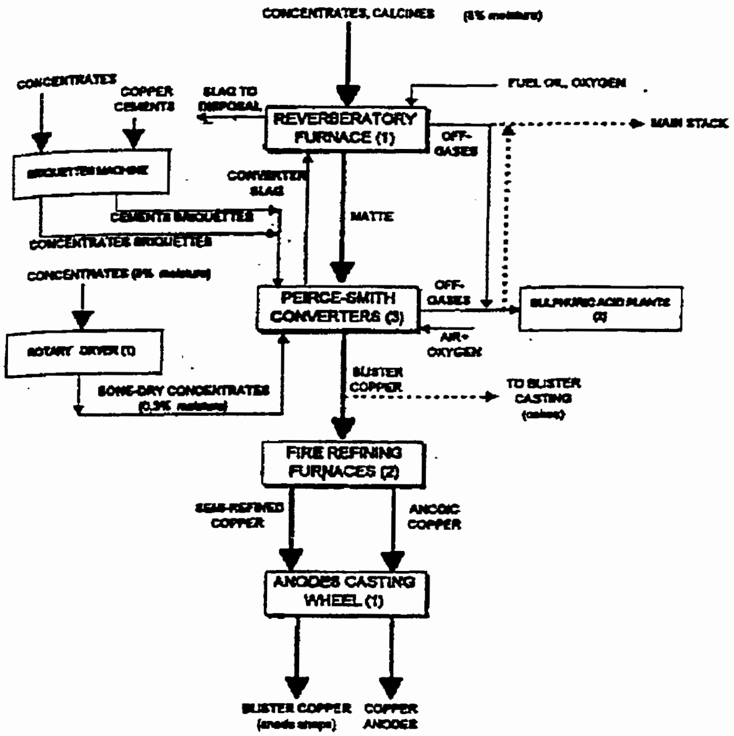


Figure 4.8. Altonorte smelter (after Campos, et al., 1998)

4.2 Environmental Situation

The main environmental problems associated to the mining sector are:

- Air pollution due to SO_2, particulate matter, and arsenic emissions.
- Water pollution due to liquid effluents containing particulate matter, dissolved metals and acids.
- Soil contamination.
- Risk posed by abandoned mining sites and tailing dams.

The metallurgical industry, principally copper smelters, is the main source of SO_2 emissions in Chile. This industry generates 92% of total SO_2 emissions in the country due to the high sulfur content of the copper ore. Chile is the tenth largest SO_2 emitter in the world (Environment Canada, 1996).

In addition to emitting SO_2, the copper smelters also release significant amounts of arsenic and particulate matter into the atmosphere (Table 4.5). There have been reductions in the amounts of SO_2, particulate matter and arsenic released into the atmosphere in recent years, but the problem remains serious.

Table 4.5. Chilean copper smelters – emissions into the atmosphere

Smelter	Emissions 1998, t/y			Reference
	Sulfur	Particulate matter	Arsenic	
Chuquicamata	101,200	1,100	1,188[1]	Queirolo, 1998; Conama, 2000
Potrerillos	150,000	N.A.	1,534[1]	Conama, 1998
Caletones	247,500	N.A.	1,440	Vega, 2000
Ventanas	12,600	N.A.	N.A.	Conama, 1998
Paipote[2]	9,086	1,389	32,4	Rojas, 2000
Chagres	6,300	N.A.	56	Duran, 1999
Altonorte	23,269	N.A.	173	Noranda, 1998
El Indio[3]	N.A.	N.A.	N.A.	
Total	549,995	-	4,423	

N.A.: Not Available

[1] Arsenic emissions in 1997, [2] Results obtained in 1999, [3] Roasting plant

4.2.1 Regulations for SO_2, Particulate Matter, and Arsenic

The Government of Chile has made environmental protection a priority. The President of Chile signed the Environmental Framework Law, known as the Basic Law (Decree Law 19,300), on March 1, 1994, establishing the National Commission on the Environment [Comisión Nacional del Medioambiente (CONAMA)] and 12 Regional Environmental Commissions [Comisiones Regionales del Medioambiente (COREMA)] to coordinate environmental protection activities among governmental agencies (Velasco, 1996).

CONAMA has the legal mandate to define Chile's environmental policy, to propose environmental regulations. CONAMA is represented in the 12 Chilean regions by the COREMA's. Each COREMA is presided by a Regional Intendant (an appointed official approximately equivalent to a U.S. Governor) and includes representatives from regional governments, the private sector, and nongovernmental organizations (NGO). The COREMA's were put in charge of the implementation and enforcement of new regulations and, through COREMA regional subsidiaries, authorize pollution prevention and abatement plans and advise the Ministry of Mining on designing environmental policies and the regulations implementing these policies, diagnosing environmental impacts, and developing general environmental objectives and policy responses.

Regulations implementing the Basic Law established equal rights and responsibilities for public and private enterprises. The Government promulgated two decrees intended to reduce fixed-source air pollution (including Decree Law 185 of 1991, which regulated sulfur dioxide emissions) and implemented regulations pertaining to the disposal of waste water from mine tailings in coastal zones (Ministerio de Minería de Chile, 1991). Decree Law 185 regulates the smelter operations that emit to the atmosphere quantities higher or equal to 3 t/d of sulfur dioxide, or 1 t/d of particulate matter. It makes it mandatory to present decontamination plans, determined demands on information reporting and, in some smelters, it forces management to report plans for controlling high SO_2 concentration episodes. It also establishes primary standards to protect the human health and secondary standards to protect the human well being from indirect causes, for example, agricultural, natural flora and fauna damages. The primary standards are described as follows:

- Particulate matter (size about 10μ): 150 μg/Nm^3, annual arithmetic mean concentration, and 80 μg/Nm^3, daily arithmetic mean concentration.

- Sulfur dioxide, SO_2: 80 μg/Nm^3, annual arithmetic mean concentration, and 365 μg/Nm^3, daily arithmetic mean concentration.

Decree Law 185 for the secondary standards applications divided Chile into two zones-the mining district (Zone 1, which covers more than half of the country, from Rancagua, site of the El Teniente smelter, to the border with Peru) for establishing the maximum emissions of sulfur dioxide and the agricultural/industrial part of the country (Zone 2, from the area south of Rancagua to Tierra del Fuego). The secondary standards for SO_2 are described as follows:

- Zone 1: 80 μg/Nm^3, annual arithmetic mean concentration; 365 μg/Nm^3, daily arithmetic mean concentration; and 1,000 μg/Nm^3, maximum concentration/hour.

- Zone 2: 60 μg/Nm^3, annual arithmetic mean concentration; 260 μg/Nm^3, daily arithmetic mean concentration; and 700 μg/Nm^3, maximum concentration/ hour.

Decree Law 165 (Regulation of arsenic emitted to the atmosphere) to be complied by the Chilean smelters, starting from June 1999 in order to protect the health of the population that lives nearby at the emission sources and to protect the surroundings. The maximum arsenic emissions allowed into the atmosphere (Table 4.6) should not exceed the standards according to the types of sources and decontamination plans of each smelter (CONAMA, 1999).

Table 4.6. Maximum arsenic allowed in the atmosphere (t/y)

Location province, region	Smelter	Copper concentrate smelting, t/y	Year		
			2000	2001	2002
Antofagasta, II	Chuquicamata	≥ 1,400,000	1,100	800	400
	Altonorte	≥ 350,000	126	126	126
Copiapó, III	Paipote	≥ 200,000	42	42	34
Chañaral, III	Potrerillos	≥ 500,000	1,450	800	150
Elqui, IV	El Indio[1]	≥ 80,000	200	200	200
San Felipe de Aconcagua, V	Chagres	≥ 350,000	95	95	95
Valparaiso, V	Ventanas	≥ 400,000	120	120	120
Cachapoal, VI	Caletones	≥ 1,100,000	1,880	375	375
Total emissions			**5,013**	**2.558**	**1.500**

[1] Roasting Plant

4.3 Sulfur Dioxide and Particulate Matter Management

The plans for reducing emissions of SO_2 and particulate matter in order to comply with the air quality rules as presented by the Chilean smelters are shown in Table 4.7 and 4.8, respectively (COCHILCO, 1998; CONAMA, 2000).

Table 4.7. Plans for reducing emissions of SO_2 by the Chilean smelters

Smelter	Sulfur dioxide emissions, t/y						
	1997	1998	1999	2000	2001	2002	2003
Chuquicamata	198,000	162,000	162,000	174,600	174,600	158,000	56,600[1]
Potrerillos	-	-	352,000	100,000	100,000	100,000	-[1]
Caletones	-	-	494,000	494,000	230,000	230,000	-[1]
Ventanas	62,000	45,000	-[1]				
Paipote	39,900	30,000	19,992	-[1]			

[1] Achievement of the regulation,

Table 4.8. Plans for reducing emissions of particulate matter by the Chilean smelters

Smelter	Particulate matter emissions, t/y						
	1997	1998	1999	2000	2001	2002	2003
Chuquicamata	3,240	3,240	3,240	1,850[1]			
Potrerillos	-	-	6,300	5,500	5,500	5,500	-[1]
Caletones	-	3,017	1,987	1,987	-[1]		
Ventanas	3,400	2,000	1,000	-[1]			
Paipote	1,500	1,000	600	-[1]			

[1] Achievement of the regulation,

The projects under development will incorporate gas handling systems and sulfuric acid plants. For example, a decontamination plan has been implemented at Codelco's smelters as follows:

- In Chuquicamata, four sulfuric acid plants began to operate from 1985 to 1998, with a total capacity around 5,600 t/d, which have allowed capturing around 87% of the sulfur and 90% of the arsenic. Additionally, a new plan that involves a second gas handling system from Peirce Smith converters and an arsenic abatement plan will allow to capture around 95% of sulfur the and 97% of the arsenic. The cost of this construction will be US$ 78 million (CODELCO, 1998).

- In 1998, the El Salvador Division completed the project of the gas handling system for the Teniente reactor and four Pierce Smith converters at the Potrerillos smelter (Figure 4.9). The cost of this construction was US$ 56 million. Additionally, outlet gases are fed to the acid plant, which began to operate at the end of 1999. The cost of this project was US$ 97 millions.

- El Teniente Division announced a two-stage plan that will involve the construction of two sulfuric acid plants. From August 1998, the first sulfuric acid plant with a capacity of 1,500 t/d and a cost of US$ 71 million, is operating at Caletones smelter, having the capability to capture 37% of the sulfur and 50% of the arsenic. The second acid plant with a capacity of 2,350 t/d is expected to be commissioned by the end of the year 2000, and it will increase sulfur recovery up to 93% (Alvarado and Godoy, 1999). Figure 4.10 summarizes the evolution of sulfur and arsenic capture and of the associated sulfuric acid production in CODELCO's operations.

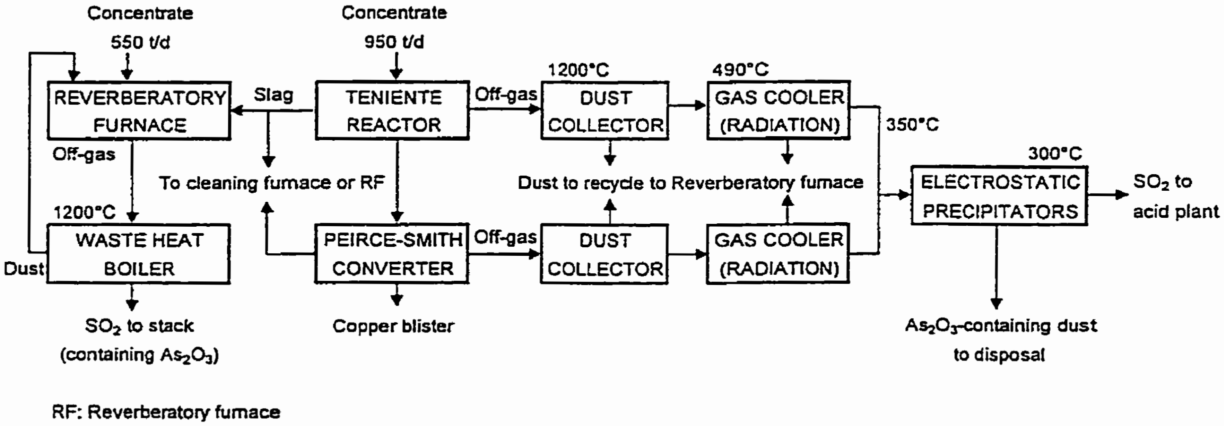


Figure 4.9. Actual gas handling system at the Potrerillos smelter
(Redrawn from Contreras, et al., 1999)

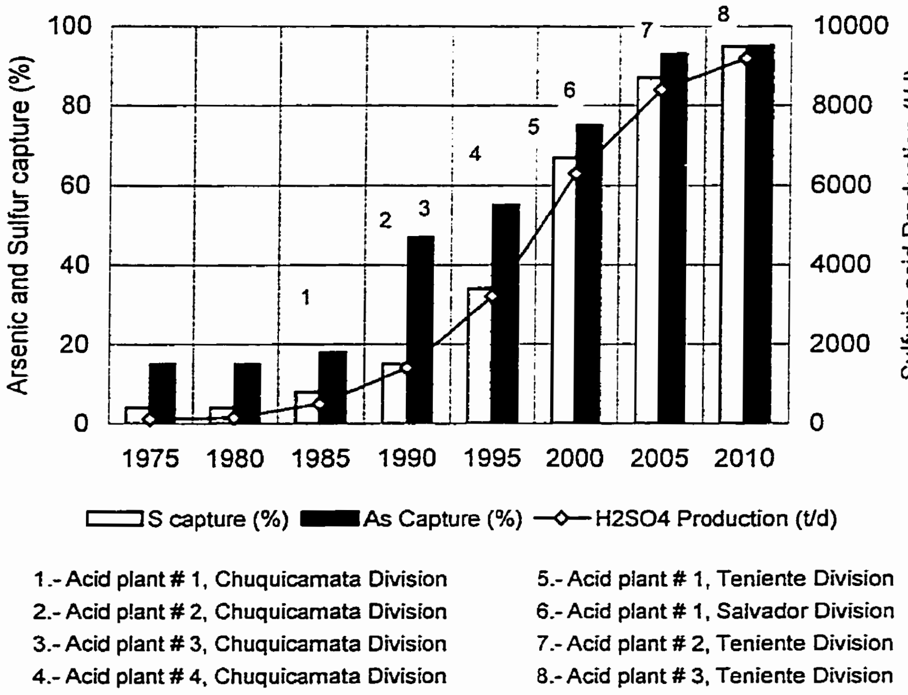


Figure 4.10. Sulfur and arsenic capture / sulfuric acid production in CODELCO-Chile smelters (after Muñoz, 1996)

4.4 Arsenic Management

In Chile, arsenic occurs principally in association with copper and gold-copper ores. The arsenic minerals present in the Chilean concentrates are shown in Table 4.9. The chemical analysis of concentrates is shown in Table 4.10.

Table 4.9. Arsenic minerals in the Chilean concentrates
(Buckingham, et al., 1999; Farias, et al., 1996; Smith, 1986)

Mineral	Formula	Concentrate
Enargite	Cu_3AsS_4	Chuquicamata, El Indio
Arsenopyrite	FeAsS	El Indio
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	El Teniente, El Indio
Realgar	As_2S_3	El Indio
Orpiment	As_4S_4	El Indio
Famatinite	$Cu_3(Sb,As)S_4$	El Indio

Table 4.10. Chemical analysis of Chilean concentrates (%)

Operation	Cu	Fe	S	As	Sb	Au g/t	Ag g/t	Bi ppm	Reference
Chuquicamata mine	28-33	28.6	30.5	0.3-1.0	0.1-0.3	-	-	30-60	Mendoza, et al., 1995
El Indio mine	23-25	18-20	32-36	8.0-8.5	0.8-0.9	15-20	250-300	-	Buckingham, et al., 1999
MM mine	35.6	17.2	33.1	4.1	0.27	-	-	-	Fan, et al., 1996
Enargite mineral[1]	41.65	8.0	32.2	12.1	-	-	-	-	Fan, et al., 1996
Ventanas smelter[2]	24-27	20-28	25-30	0.14-0.18	0.01	-	-	10	Díaz, et al.. 1997
Caletones smelter[3]	31-33	21-25	29-32	0.23-0.35	0.012-0.02	-	-	N.A.	Achurra, 1999; Vega, 2000

[1] Obtained from CODELCO's MM mine, [2] Concentrate blend to the Teniente reactor, [3] Average between Jan. 99- Apr. 2000
N.A.: Not available

The MM mine, otherwise known as Mansa Mina ("MM"), is a copper orebody located between Chuquicamata mine and Calama City, with geological resources between 650 and 900 million tons averaging 1.3% copper, but high arsenic content obstructs its exploitation by pyrometallurgical route (Mining Magazine, 1992).

4.4.1 Present Solutions

In Chile, the only production of arsenic is in the form of arsenic trioxide, which is a by-product of the copper concentrate produced at the El Indio mine, while El Teniente and Chuquicamata smelters have arsenic treatment plants, where it is disposed of in the form of ferric arsenate. Also, all the smelters have effluents treatment plants for the arsenic disposal either as ferric arsenate or calcium arsenate/arsenite.

- **El Indio Recovery Plant**

Roasting has been applied since 1981 at El Indio mine in Chile for arsenic trioxide recovery and thus making its concentrate more acceptable as smelter feed (Figure 4.11). The 3 roasters are 14 hearth, 6.5 m diameter Nicols Herreshoff units. Each is fed at 6.5 to 7 t/h via a weightometer belt, and double sealing flapgates on top of each roaster. In the upper six hearths, air is injected to allow slightly oxidizing conditions, resulting in an exothermic reaction between the contained arsenic and sulfur. The temperature profile is maintained at between 630° C and 720° C, throughout the roaster. In the lower hearths (7 to 14), the conditions are kept strongly reducing, resulting in fuming off As_2S_3 and Sb_2S_3, and elemental sulfur. The calcine, is discharged through a grizzly screen, cooled in water-jacketed screw conveyors, wetted for handling and stored in a covered shed for shipment by truck to local smelters or to the port *en route* to smelters.

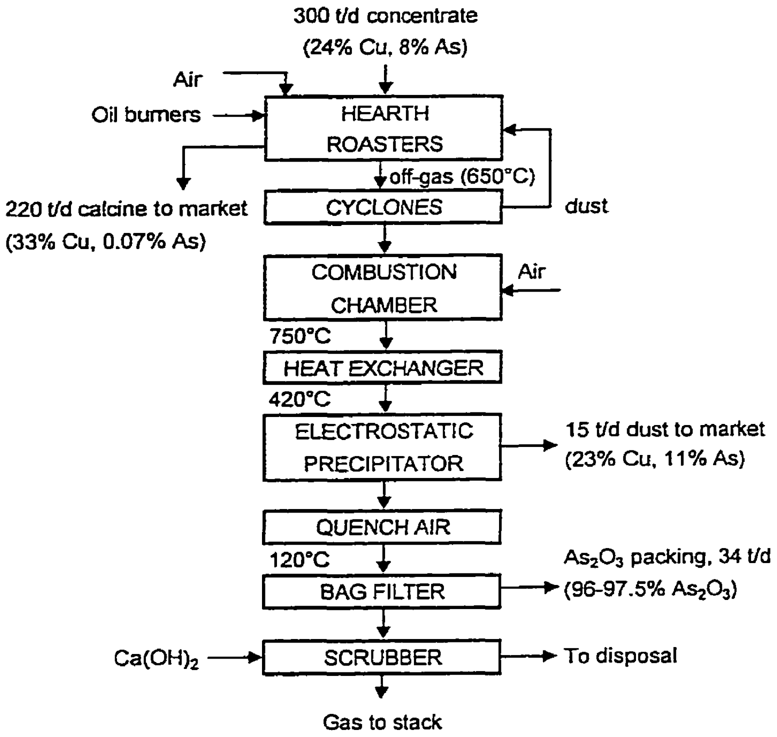


Figure 4.11. El Indio roasting plant (after Buckingham, et al., 1999)

Roaster extraction (Table 4.11) of arsenic and antimony have been about 95% and 45% respectively, while about 42% of the original sulfur content is allowed to remain in the calcine (Smith, et al., 1985; Smith and Paredes, 1988).

Table 4.11. El Indio roaster extraction of As, Sb, and S (%)

Element	Feed	Calcine	Extraction
As	7.2	0.48	94.5
Sb	0.54	0.36	44.5
S	34.4	24.9	42.4

Off-gas is passed through cyclones to remove dust, and then is drawn off through a combustion chamber where air is added to convert arsenic sulfide, antimony sulfide and elemental sulfur to their oxides at a temperature of 750°C. These gases are then cooled in a heat exchanger to approximately 350°C and the dust, containing As_2O_3 and Sb_2O_3 is removed in an electrostatic precipitator. The captured dust is mechanically conveyed from the bottom of the electrostatic precipitator to storage silos prior to wetting and truck transport to market (Buckingham, et al., 1999). The gas discharge from the electrostatic precipitator is further cooled to 120°C with quenched air to collect sublimed arsenic trioxide in a bag house and subsequently packaged for sale to chemical manufacturers in the US. The filtered gas is discharged to the atmosphere through a stack located approximately 100 m up the hill from the plant (Jeffrey, 1996).

In 1997, the plant installed a wet lime scrubber to remove trace amounts of As_2O_3 and particulate matter from the stack gases before disposal. Isocinetic studies in the stack showed that arsenic recovery efficiency, increased from 95%, depending on bag house efficiency, which ranged between 80% to 96%, to about 98% (Valenzuela, 1999).

El Teniente Disposal Plant

This plant processes dust collected by the electrostatic precipitators of gas handling system at the Caletones smelter (Table 4.12). The dust is slurried with solution rich in H_2SO_4 obtained from El Teniente solvent extraction plant and transported by special truck to the plant (Vuskovic, 1996).

Table 4.12. Dust chemical composition (Araya, 1999)

Cu_T	Cu insol	As_T	Fe_T	Bi_T	$As^{(III)}$	$As^{(V)}$	Fe^{3+}	Mo	Sb
24.0	13.0	6.8	3.8	0.55	6.5	0.3	3.4	0.9	1.5

The process (Figure 4.12) comprises three stages:

1. Acid leaching: In this stage, slurry is leached with sulfuric acid for 15 minutes, at room temperature to extract copper and arsenic. The solution is passed to the arsenic precipitation stage.

2. Bismuth leaching: The solids from the first stage are leached with H_2SO_4 (40 g/L) containing NaCl (150 g/L) for 60 minutes, and a liquid/solid ratio of 1.5/1. The slurry is then transferred to a thickener, the overflow contains bismuth, copper, arsenic, and other metals, and the solids are washed in another thickener with sulfuric acid and solution from SX plant, then recycled to the smelter. If the economic situation permits, bismuth can be recovered from solution. If not, it is mixed with the first solution and treated further as shown below (Araya, 1999).

3. Arsenic precipitation: When bismuth is not recovered, the overflow of both thickeners, is mixed and treated with a 30% solution of H_2O_2 (12 L/m^3) to oxidize As(III) to As(V), NaOH is added to adjust pH to 3, then ferric sulfate is added to precipitate ferric arsenate. Finally, the precipitate is thickened. The overflow is sent to the solvent extraction plant for copper extraction, and the solids, containing ferric arsenate and bismuth, are disposed of into the landfill.

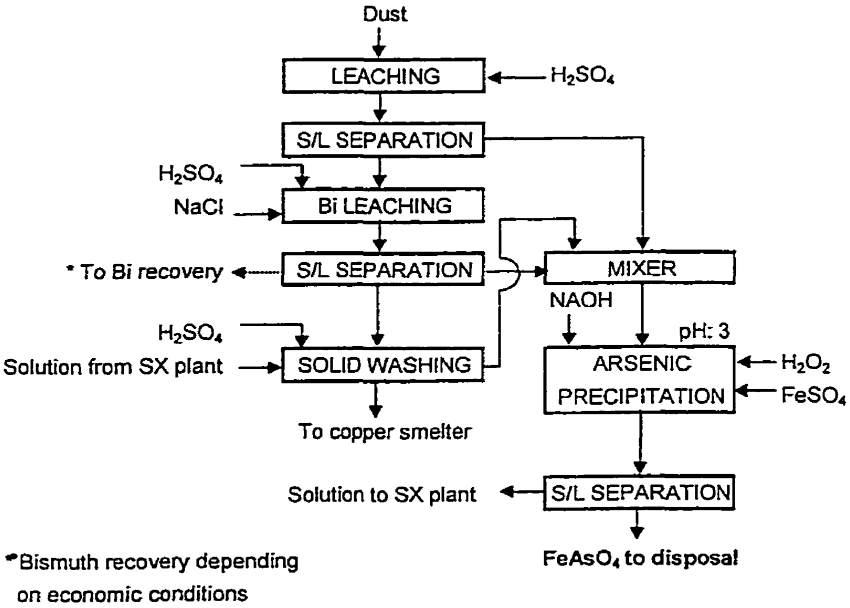


Figure 4.12. El Teniente plant for treatment of smelter dust (after Vuskovic, 1996)

Also, arsenic-containing effluents generated by the sulfuric acid plant are treated in a effluent treatment plant, where the solution is neutralized and arsenic is precipitated as calcium arsenite, $CaAsO_2OH$, and arsenate, $Ca_2AsO_4(OH)$, followed by calcination to produce a stable product, $Ca_3(AsO_4)_2$, (Vega, 2000).

- **Chuquicamata Disposal Plant**

Chuquicamata Division also treats smelter dusts in a hydrometallurgical plant (Figure 4.13) recovering copper and disposing of the arsenic in the residues of the leaching operations where it will precipitate *in situ* as ferric arsenate (Farias, et al., 1996).

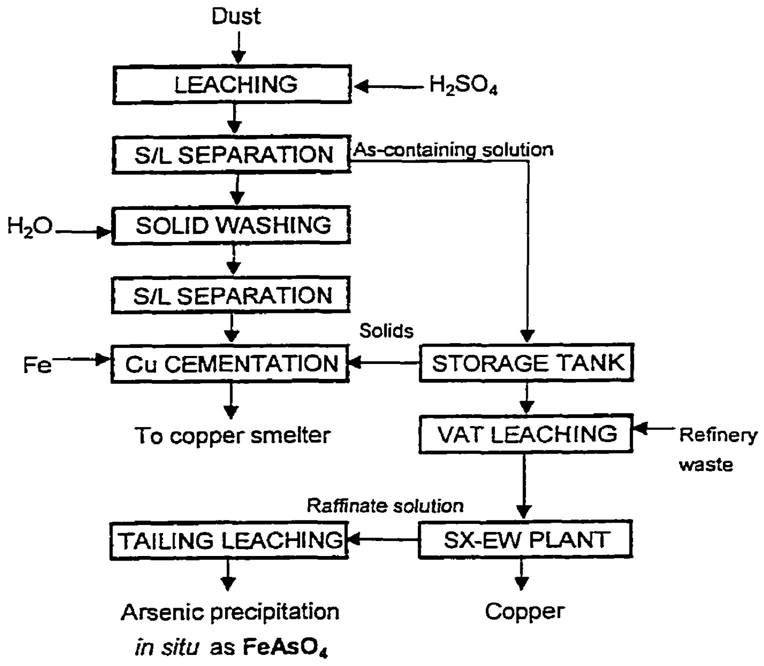


Figure 4.13. Chuquicamata plant for treatment of smelter dust (after Farias, et al., 1993)

Also, the effluent generated in the sulfuric acid production at Chuquicamata smelter is neutralized to pH 12 and arsenic is precipitated as calcium arsenite, $CaAsO_2(OH)$. The slurry is then transferred to a thickener, the overflow containing the clean water to pH 12 is recycled to the industrial water system, and the solids are filtered to obtain a cake (50,000 m^3/y), containing 3 to 6% As and 30 to 45% H_2O, is transported by special trucks to be disposed of into the landfill (Pedreros, 1998). Variations of this process are used at Paipote, Chagres and Altonorte smelters (Rojas, 2000).

- **Potrerillos Effluent Treatment Plant**

The effluent (30 m^3/h) of the sulfuric acid plant containing 26 g/L H^+ and 10 g/L As is neutralized with milk of lime to pH 11 and arsenic is precipitated as calcium arsenate/arsenite (Figure 4.14). The slurry is thickened, the underflow is filtered, and the cake (4 t/h) containing 40% H_2O is sent to disposal. The overflow containing 100 ppm As is neutralized further to pH 8 and arsenic is precipitated as ferric arsenate. The slurry is then transferred to another thickener where the underflow is filtered and the overflow is passed by a sand filter to obtain finally a treated effluent containing < 1 mg/L As (Rojas, et al., 1999).

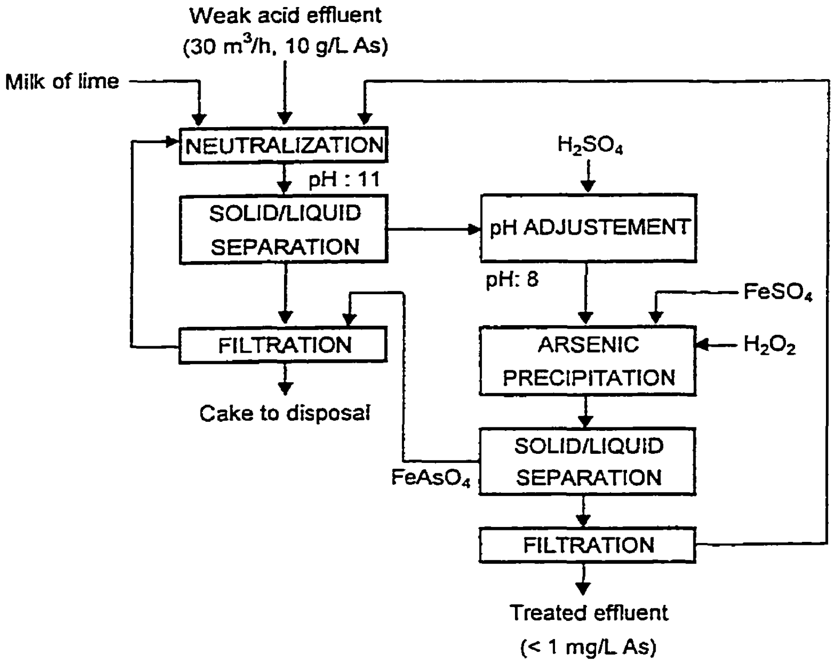


Figure 4.14. Potrerillos plant for treatment of effluents (after Lange, 1999)

CHAPTER V

ARSENIC RECOVERY WORLDWIDE

As it was shown in Table 2.6 (Chapter II), there are several countries recovering arsenic from gold ores, copper and cobalt concentrates or arsenic-bearing copper smelter dusts. However, information about most of these operations is not available in the literature (e.g., China, Peru, Bolivia, Morocco, Belgium, France, Georgia, etc.).

5.1 From Copper Concentrates

5.1.1 Sodium Sulfide Leaching

Sodium sulfide leaching has been successful in selectively recovering arsenic from copper concentrates then precipitating it as copper arsenate.

- **Equity Silver Mines Process**

Equity Silver Mines Limited (Houston, British Columbia) designed, built and operated a leach plant for a numbers of years to reduce the levels of antimony and arsenic in its copper concentrate (Edwards, 1985). The antimony (2%) and arsenic (0.5%) from the flotation concentrate were leached and recovered as by-products (Figure 5.1). Flotation concentrate (90 t/d) was slurried with hot alkaline sodium sulfide solution and leached for 8 hours in heated tanks at about the boiling point:

$$HS^- + OH^- \rightarrow S^{2-} + H_2O \tag{5.1}$$

$$3Cu_2S \cdot Sb_2S_3 + 3S^{2-} \rightarrow 3Cu_2S \text{ (insoluble)} + 2SbS_3^{3-} \text{ (soluble)} \tag{5.2}$$

$$3Cu_2S \cdot As_2S_3 + 3S^{2-} \rightarrow 3Cu_2S \text{ (insoluble)} + 2AsS_3^{3-} \text{ (soluble)} \tag{5.3}$$

Sodium antimonate, was obtained by autoclave oxidation of the leach liquor by oxygen at 700 kPa and 145°C:

$$2SbS_3^{3-} + 7O_2 + 2OH^- + 5H_2O \rightarrow 2Sb(OH)_6^- + 3S_2O_3^{2-} \tag{5.4}$$

$$2AsS_3^{3-} + 7O_2 + 6OH^- \rightarrow 2AsO_4^{3-} \text{ (soluble)} + 3S_2O_3^{2-} + 3H_2O \tag{5.5}$$

$$2S^{2-} + 2O_2 + H_2O \rightarrow S_2O_3^{2-} + 2OH^- \tag{5.6}$$

$$2SbS_3^{3-} + 13O_2 + 8OH^- + 2H_2O \rightarrow 2Sb(OH)_6^- + 6SO_4^{2-} \tag{5.7}$$

$$2AsS_3^{3-} + 13O_2 + 12OH^- \rightarrow 2AsO_4^{3-} \text{ (soluble)} + 6SO_4^{2-} + 6H_2O \tag{5.8}$$

$$S^{2-} + 2O_2 \rightarrow SO_4^{2-} \tag{5.9}$$

The sodium antimonate by-product had the following specifications:

Sb	47%	Minimum
Cu	50	ppm maximum
As	500	ppm maximum
Moisture Content	12.5%	maximum

Initially, arsenic in solution was disposed of as calcium arsenate by autoclave oxidation at 1400 kPa and 150°C followed by precipitation with lime. A marketable, high-purity copper arsenate was later produced by treating the solution with $CuSO_4$ (Figure 5.1). Arsenic autoclaving proceeded according to these simplified equations:

$$2AsO_4^{3-} + 3Ca(OH)_2 \rightarrow Ca_3(AsO_4)_2 \text{ (insoluble)} + 6OH^- \tag{5.10}$$

$$SiO_2 + 2Ca(OH)_2 \rightarrow Ca_2SiO_4 \text{ (insoluble)} + 2H_2O \tag{5.11}$$

$$S_2O_3^{2-} + 2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + H_2O \quad (5.12)$$

$$SO_4^{2-} + Ca(OH)_2 \rightarrow CaSO_4 + 2OH^- \quad (5.13)$$

$$2S^{2-} + 3O_2 + 4OH^- \rightarrow 2SO_4^{2-} + 2H_2O \quad (5.14)$$

Development of the copper arsenate circuit was cut off by the economically driven cessation of the leaching operation in 1984 (Edwards, 1991). The final liquor was a high-purity caustic solution of sodium sulfate from which the saltcake was removed in a continuous crystallizer-centrifuge-dryer train.

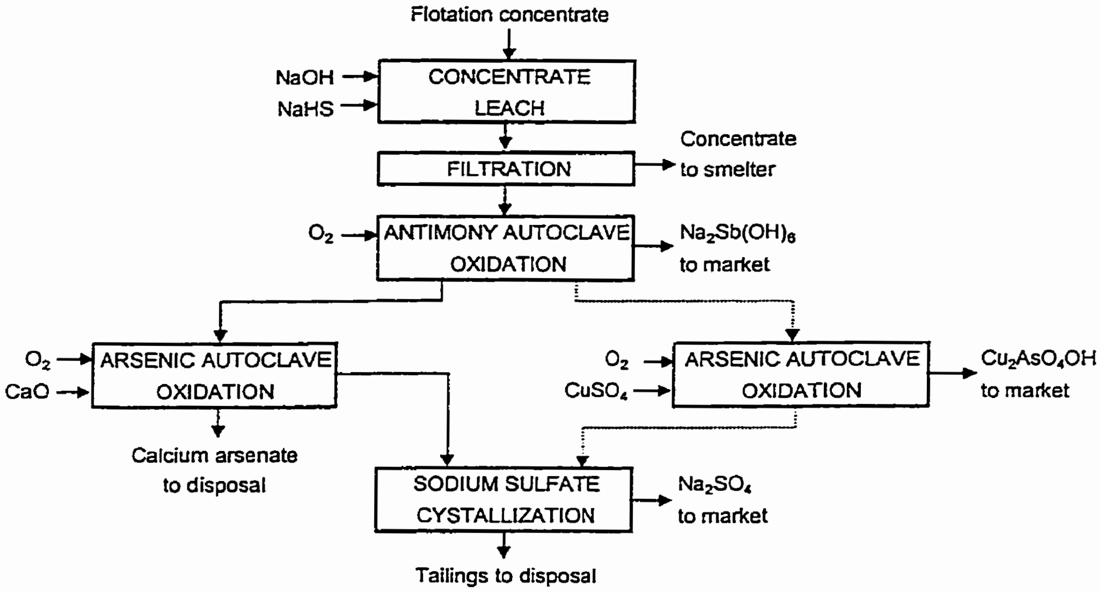


Figure 5.1. The Equity Silver leach plant (after Edwards, 1991).

5.1.2 Roasting

Roasting has been applied since 1981 at El Indio mine in Chile for As_2O_3 recovery as mentioned earlier in chapter 4. The roasting plant using 3 multiple hearth furnaces has a throughput of 300 t/d and an As_2O_3 production of 30 t/d (Buchingham, et al., 1999). In Namibia, the copper concentrate produced at Tsumeb mine, having 6-7% arsenic, is also treated prior to the smelter in an arsenic plant consisting of four roasters with condensing chambers and a common bag house. The arsenic plant produces 99% pure arsenic trioxide. In

1998, its production was 1,800 tons. The Tsumeb Copper Company however, was liquidated in 1998 (Coakley, 1999). In Philippines, the copper concentrate produced at Lepanto plant is treated at the PASAR smelter by means of fluidized bed roasting, producing 2,000 t/y of white arsenic and a calcine having 1% As (Piret and Melin, 1989). However, the Lepanto Mining Company closed its plant in 1997 due to the exhaustion of its ore (Lyday, 1998). Sweden was a important producer of As_2O_3 from copper concentrates by means of fluidized bed roasting at Boliden Rönnskär smelter (Lindkvist and Holmström, 1983). Production was 10,000 t/y but it was eventually decreased to 2,500 t/y in 1991. Finally, production ceased at the end of 1991 due to environmental reasons (Loebenstein, 1992). In the United States, most arsenic was recovered from copper concentrates for sale between 1910 and 1985, after which all domestic production of arsenic ceased when ASARCO, the sole remaining producer, closed its copper smelter and associated arsenic plant in Tacoma (Loebenstein, 1994). In this plant, the copper concentrate, having 4% As, was roasted prior to smelting and arsenic was then captured using electrostatic precipitators and condensing chambers. The final product was a crude As_2O_3 of minimum 95% purity (Edelstein, 1994).

5.2 From Gold Concentrates

Several gold mines produced and roasted a sulfide flotation concentrate in their gold extraction processes to recover arsenic trioxide as it is shown in Table 5.1.

Table 5.1 Operating results in gold concentrate roasting plants

Operation	Country	Stages	Feed (t/d)	Feed, %		Calcine, %		Extraction, %		As_2O_3 t/d	Reference
				As	S	As	S	As	S		
Cochenour Williams	Canada	1	15	6.3	18.4	1.3	1.6	84	93	N.A.	Piret and Melin, 1989
Dickenson Ltd	Canada	1	12-16	8	20-36	N.A.	N.A.	N.A.	N.A.	N.A.	Gagan, 1979
Campbell Red Lake	Canada	2	60	7-9	17-18	1.0	1.6	81	96	6.3	Frostiak and Haugrud, 1995
Giant Yellowknife	Canada	2	130	7-9	20.2	1.0	2.5	89	88	N.A.	Piret and Melin, 1989
Kerr Addison Ltd	Canada	1	N.A.	1	42	N.A.	N.A.	N.A.	N.A.	N.A.	Gagan, 1979
Lancefield Wastern	Australia	1	400	1.4	24	N.A.	N.A.	N.A.	N.A.	N.A.	Brown, et al., 1990
New Consort Mine	South Africa	2	96	2-3	32-40	1.0	0.6	88	92	2.5	Penman, 1985; Ferreira, et al., 1989

N.A.: not available

5.2.1 Canadian Operations

There was virtually no market for this product in Canada prior to 1977 and the arsenic trioxide was stored underground in sealed stopes. Improved market conditions gave an incentive to the companies for the production of a high arsenic trioxide, which was sold.

- **Giant Yellowknife Mines Ltd**

In this plant (Figure 5.2), the flotation concentrate was roasted in a two-stage fluosolid roaster (More and Pawson, 1978). The hot gas was directed to two cyclones in series to remove the coarse dust particles, which were added to the calcine, and then it was leached with cyanide solution for residual gold recovery. The hot gas, along with the remaining dust, proceeds to the electrostatic precipitators where the fine dust was removed. The cleaned gas was then cooled to 110°C using air. Sublimation produced impure arsenic trioxide dust, which was removed by a bag filter and pneumatically pumped to underground storage vaults or sold. Electrostatic precipitator dust because of its high arsenic content and other impurities was treated in an activated carbon batch process for gold absorption (Gagan, 1979).

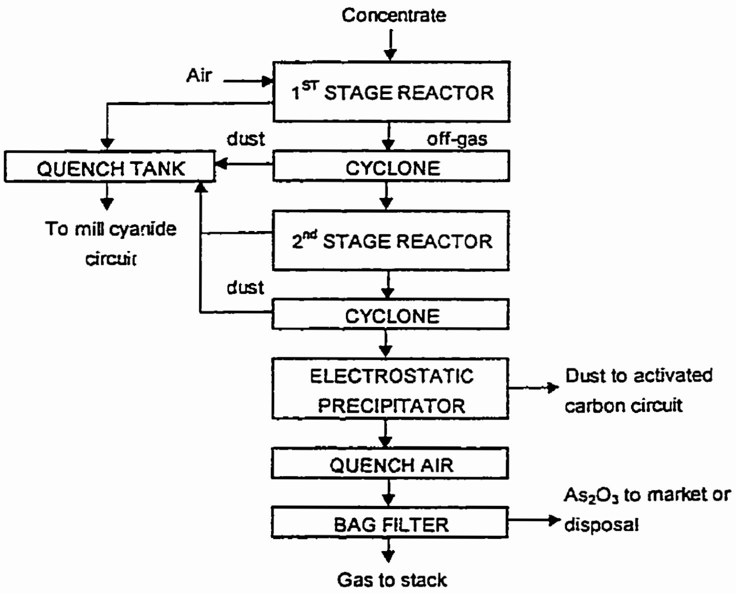


Figure 5.2. Giant Yellowknife Mines Ltd. roasting plant (after Gagan, 1979)

- **Campbell Red Lake Mines Ltd**

A 14-ft. roaster was installed at this mine in 1949. The reactor operated as a single stage roaster until 1956 when a second roasting stage was added to improve gold recovery (95%) (Maycock, et al., 1990). Flotation concentrate was then treated in a two stage fluid bed roasting circuit, similar to the circuit of Giant Yellowknife mines. The first roaster was operated at 540 to 565°C and most of the arsenic and sulfur were oxidized and volatilized in this unit. The products from the first roaster, both solids and gases, were passed to the second roaster which was operated at 520 to 525°C and which ensured the maximum elimination of arsenic and sulfur from the calcine. Solids were recovered from the roaster gases by two parallel sets of three stage cyclones, operated at 400°C, and by electrostatic precipitators, consisting of two units in parallel, each with two chambers. These units operated under conditions, which avoided arsenic trioxide condensation. The roaster gas was then mixed with air to cool it to approximately 107°C and to condense out particulate arsenic trioxide. It was then captured in a chamber bag house before the gas was discharged to the stack. The arsenic trioxide was then sold or conveyed to an underground storage vault (Frostiak, et al., 1990). However, in 1991, due to environmental reasons, the existing roaster operation was shut down and a pressure oxidation plant was built. In the autoclave, arsenic was solubilized and then precipitated as ferric arsenate (Frostiak and Haugrud, 1995).

- **Dickenson Mines Ltd**

A 6 ft single-stage fluid bed roaster was installed at the Dickenson Mines in 1951 (Figure 5.3) (Maycock, et al., 1990). The concentrate was roasted at 705-760°C. The calcine, was quenched, dewatered, conditioned with sodium cyanide and lime and finally pumped to the cyanide circuit to recover the gold (Malloy and Tapper, 1978).

Off-gas was passed through cyclones to remove coarser dust. The gas was then cooled in a heat exchanger to approximately 315°C. The cooled gas was passed through two hot fabric filter bag houses in parallel to remove the remaining suspended particulate matter. These were added to the dust recovered in the cyclones and the calcine from the roasting operation. The gas discharge from the filter bag houses was further cooled to 145°C with quenched air to collect sublimed arsenic trioxide in two fabric bag houses and subsequently packaged for sale. The filtered gas was then passed through an additional clean-up fabric filter bag house operated at 123°C. The clean gas entered the heat exchanger, where it was reheated, and then was discharged to the atmosphere through a stack (Gagan, 1979).

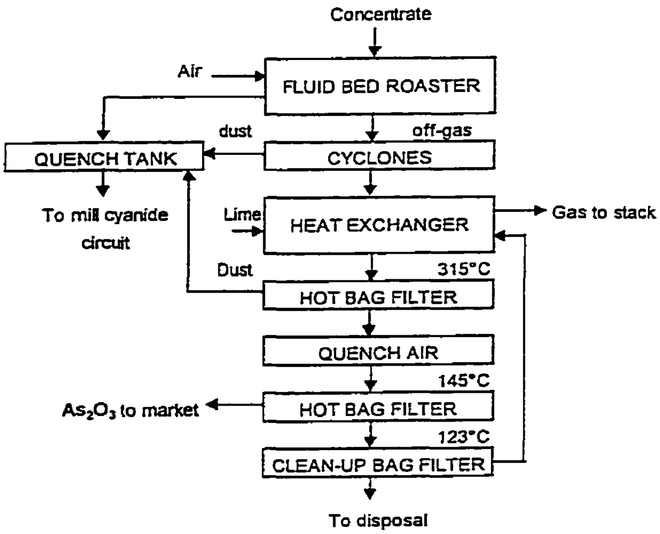


Figure 5.3. Dickenson Mines roasting plant (after Gagan, 1979)

A roasting plant also operated at Kerr Addison Mines for three months per year, during the winter. The concentrate containing about 1% As, 42% S and 0.6 oz/t of gold was roasted at 370°C in a single-stage fluid bed reactor. Off-gas was cooled to about 290°C by passing it through a waste heat boiler, then directed through two cyclones in series to capture the coarser dust. The cyclone exhaust gas was discharged to the atmosphere through a stack. Calcine from the roaster, boiler and cyclones was water quenched and pumped to the cyanide circuit for residual gold recovery (Gagan, 1979).

In the early 1980's, Cominco (operating in Yellowknife of the Northwest Territories of Canada) built and operated a plant for a numbers of years at the Con gold mine, producing arsenic trioxide crystals by roasting and recovering gold values. Metallurgical complexities and a collapse of the market for the As_2O_3 crystals resulted in the plant closure in 1989 (MIRAMAR, 2000).

In South Africa, Eastern Transvaal Consolidated Mines (ETC) built a fluid bed roasting plant in 1983 to treat gravity and flotation concentrates from Sheba and Agnes mine, and gravity concentrates from New Consort mine. Throughput was 34 m/d and sulfur dioxide from the combustion of sulfides discharged through a stack. To accommodate increasing production, a new roasting plant similar to the Giant Yellowknife operation in Canada was built in 1988 to treat 100 t/d mixed concentrates. To reduce atmospheric pollution, the roasters were coupled to a sulfuric acid plant that produced 100 t/d (Ferreira, et al., 1989)

5.2.2 Australian Operations

Either white arsenic or arsenic-bearing gold concentrate has been produced in each of the Australian states with the exception of Tasmania and the Northern Territory (Minfact, 1995a). Small quantities of arsenic trioxide were produced in South Australia and in New South Wales (NSW) prior to 1912, however prices were low and no further production ensued until an improvement in the market price and a strong demand in Queensland for arsenic, for prickly pear poison, resulted in major production in several states within the period 1916-1936.

Almost two-thirds of the Australian arsenic production came from the Wiluna Gold Mine in the Western Australia, where an arsenic plant was constructed in 1931 to treat the high arsenopyrite-containing gold ores. The concentrate was roasted and arsenic was collected in condensing chambers and finally, in an electrostatic precipitator, then the crude arsenic was refined in a mechanical furnace. Production ceased in 1949 because the ore bodies were exhausted, however dump material was retreated in the following two years. Other important producers in Western Australia were the Transvaal (Jupiter) Mine and Ingliston Consols Extended Gold Mine, but no refining of arsenic took place on site.

Arsenic deposits in South Australia were small representing only a minor proportion of the total Australian production. The two sources of recorded production come from the Callington

District and the Talisker Mine. All of the ore was treated outside the state as the output was not sufficient to warrant installation of recovery plants. In Victoria, refractory arsenical ores were treated at two metallurgical plants in Bendigo, Leggo and Liddell, and also at a metallurgical plant at Ballarat. These plants recovered arsenic from concentrates purchased from Victoria gold mines, and also from interstate mines. None of the Victorian mines had a large output of arsenical ore. In Queensland, the entire arsenic output has come from the Stanthorpe district. The largest mine was the Jibbinbar Mine, which was operated by the Queensland State Government since 1919 for the sole purpose of producing cheap arsenic for the manufacture of prickly pear poisons. A reverberatory furnace was in operation to treat the ore that came directly from the mine. The flue product without refining contained an average of about 90% of arsenic trioxide, and in this form it was marketed.

In New South Wales, arsenic ores have been recovered at eight main plants. The New England region was the most important area of the State, accounting for 85% of total production. The Ottery and Mole River mines were the State's main arsenic producers. These were the only two mines in the State equipped with a plant capable of producing refined arsenic trioxide (99.7%). The Mole River mine (Roberts Chemicals Ltd) operated furnaces and flues for the production of white arsenic and arsenic pentoxide. The treatment plant was of considerably different design to that at the Ottery mine (Figure 5.4), having no series of condensation chambers, simply one long flue leading to the stack.

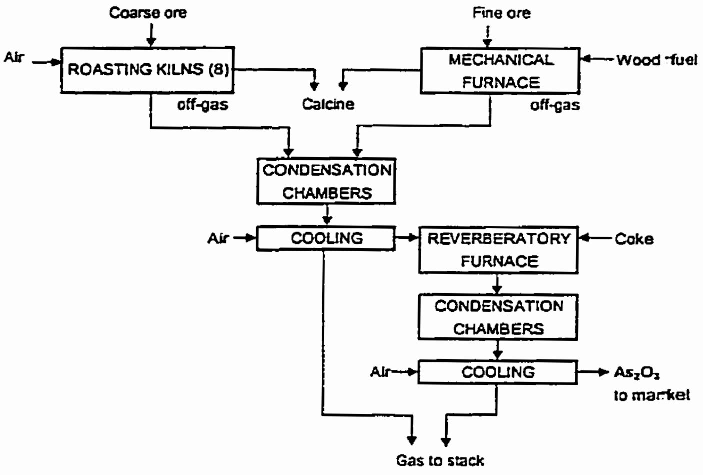


Figure 5.4. Arsenic plant at Ottery mine (from Minfact, 1995b).

5.3 From Copper Smelter Dusts

Arsenic may be recovered as refined arsenic trioxide from dusts that accumulate as an intermediate product in the smelting of arsenic-bearing concentrates, principally from copper smelters.

- **Arsenic Trioxide Processes**

Japan's copper smelters have recovered arsenic from smelter dusts. In the 1980's, the Furukawa Company produced 300 t/y of As_2O_3 at its Ashio copper smelter (Brewis, 1984). However, Furukawa permanently closed its smelter in 1988 (Wu, 1999). The Sumitomo Metal Mining Company also produced As_2O_3 at its Toyo copper smelter. The arsenic plant went into operation in 1983 and it had the capacity to produce 720 t/y of 99.9% pure As_2O_3 (Terayama, 1999).

At the Toyo smelter, the arsenic contained in the concentrates fed to the smelter is volatilized in the off-gas, and absorbed in the scrubbing liquor in the cooling tower ahead of the acid plant. The scrubbing liquor is pumped to the gypsum plant, where the arsenic is fixed as sulfide. This arsenic sulfide precipitate is the feed to the process (Figure 5.5).

Copper oxide obtained from the Niihama nickel refinery is converted to copper sulfate by aeration leaching with sulfuric acid, and is recycled from the substitution and reducing process. Arsenic sulfide filter cake is repulped and heated to 70°C in the $CuSO_4$ solution. At this temperature As_2S_3 reacts with the copper sulfate to form copper sulfide, while the arsenic is dissolved as arsenious acid according to:

$$As_2S_3 + 3CuSO_4 + 4H_2O \rightarrow 2HAsO_2 + 3CuS + 3H_2SO_4 \qquad (5.15)$$

Arsenic trioxide is precipitated from arsenious acid solution by cooling at 25°C:

$$2HAsO_2 \rightarrow As_2O_3 + H_2O \qquad (5.16)$$

The slurry is filtered, the filtrate recycling to the gypsum plant. The filter cake is next repulped with copper sulfate solution, and is passed to the oxidizing leach stage. The slurry is then heated once more by steam injection to 70°C in tanks equipped with high-powered agitators and air injectors to oxidize As (III) to the more soluble As (V) form:

$$2HAsO_2 + O_2 + 2H_2O \rightarrow 2H_3AsO_4 \qquad (5.17)$$

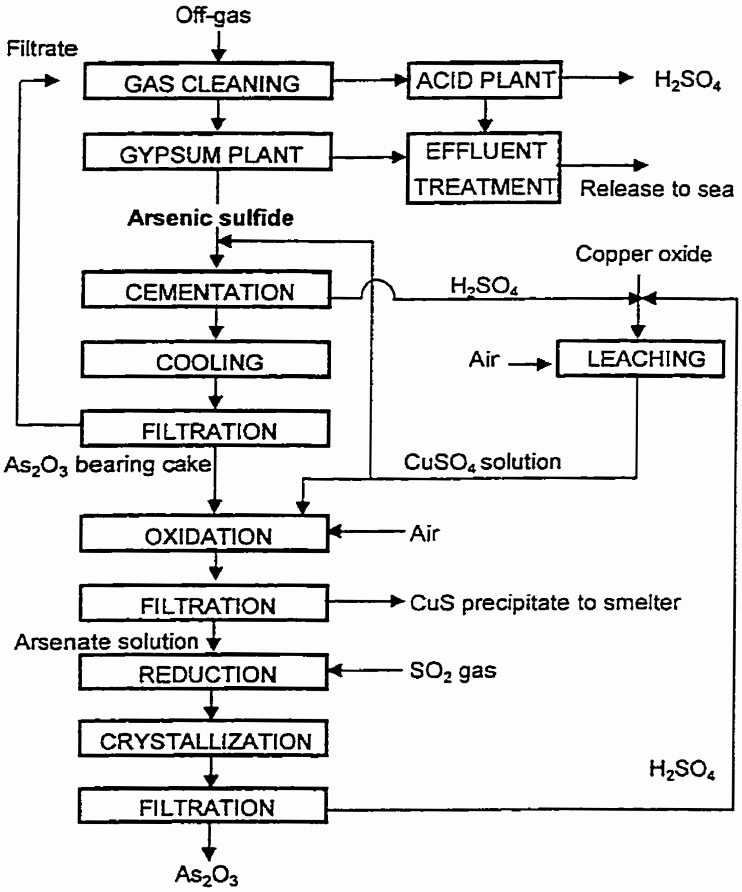


Figure 5.5. Production of As_2O_3 at Toyo smelter (after Terayama, 1999)

Total arsenic concentration in oxidized solution is controlled at 60 - 70 g/L of which As (III) is held to less than 15 g/L. The accompanying copper sulfide, however, is not affected by this oxidation process, and remains as a solid. The oxidized slurry is filtered and CuS filter cake is washed and returned to the smelter.

The solution is then reduced by SO_2 to precipitate arsenic trioxide:

$$2H_3AsO_4 + 2SO_2 \rightarrow As_2O_3 + 2H_2SO_4 + H_2O \qquad (5.18)$$

Sulfuric acid generated is recycled to the copper leaching step. Crystals of As_2O_3 are dehydrated in a centrifuge to a moisture content of 2 to 3%. Finally, they are packed and shipped after drying with fully sealed rotary disc drier to a moisture content of 0.1% or less. The dried crystals are automatically weighed and packed into steel drums, each holding 100 kg. Table 5.2 shows typical analysis of As_2O_3 (Toyabe, et al., 1988).

Table 5.2. Typical analysis of As_2O_3 (ppm)

As_2O_3	Fe	Cu	Zn	Se	Sb	Te	Pb	Bi	Ca	C
99.9%	<1	7	1	<1	110	<1	<1	<2	<1	<0.01%

The production cost of Sumitomo's process is high because 2.6-3 tons of copper oxide are required to produce one ton of arsenic trioxide. Arsenic recovery is very low, about 55% because of recycling. Also, the operating conditions are complicated because of its high temperature, high slurry and sulfuric acid concentrations, and their long reaction periods: cementation time, 4 h; oxidation time, 10 h (Kaixi, et al., 1998).

In China, a smelter also uses the cementation flowsheet to treat arsenic sulfide residues (Haibei, 2000). They have a small plant to produce $CuSO_4$ from CuO powder, which reacts with As_2S_3 according to:

$$As_2S_3 + 3Cu^{2+} + 4H_2O \rightarrow 2HAsO_2 + 3CuS + 6H^+ \qquad (5.19)$$

To simplify the Sumitomo's process, Beijing General Research Institute of Mining and Metallurgy has developed an aqueous oxidation process (Figure 5.6) using oxygen at 150° C and 550 kPa to leach arsenous sulfide residues from Guixi smelter. Experimental results show satisfactory arsenic and copper extraction, 97.7 and 97.4%, respectively (Kaixi, et al., 1998).

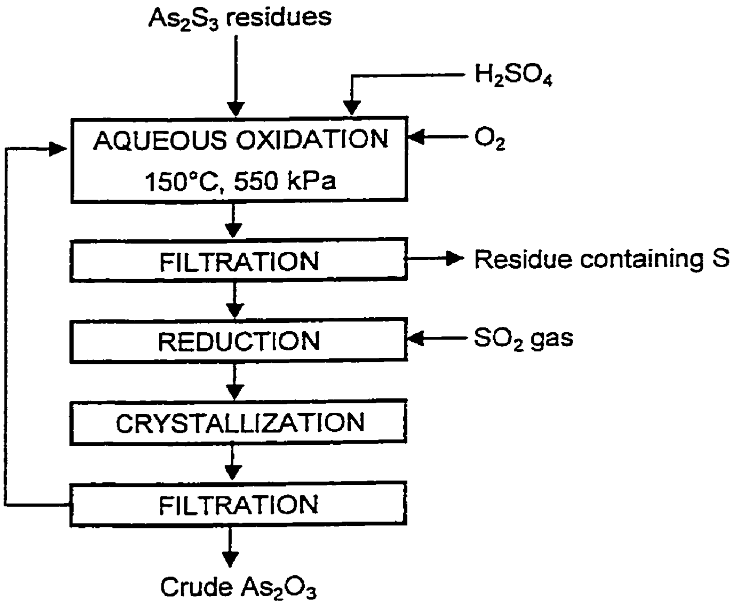


Figure 5.6. Production of As_2O_3 by aqueous oxidation process (after Kaixi, et al., 1998)

- Aqueous oxidation reaction can be described as follows:

$$2As_2S_3 + 5O_2 + 6H_2O \rightarrow 4H_3AsO_4 + 6S^\circ \qquad (5.20)$$

The slurry is filtered and the residue containing sulfur can be recycled to the feed material preparation of smelting. The filtrate is then reduced by SO_2 to produce crude arsenious acid:

$$H_3AsO_4 + SO_2 \rightarrow HAsO_2 + H_2SO_4 \qquad (5.21)$$

from which As_2O_3 is obtained by further cooling and crystallization:

$$HAsO_2 \rightarrow As_2O_3 + H_2O \qquad (5.22)$$

Sulfuric acid generated is recycled to the aqueous oxidation stage and crude As_2O_3 is then refined.

- **Arsenic Metal Processes**

Sumitomo Metals Mining also developed in 1984 a purification technique to produce 18 t/y of high purity arsenic metal from arsenic trioxide to fulfill the demand of semiconductor field (Toyabe, et al., 1988). Figure 5.7 shows the process flowsheet. In this process As_2O_3 is dissolved in a mixture of HCl and conc. H_2SO_4, which acts as a dehydrating agent. The sulfuric acid is added more than 1.6 times as much as the arsenic trioxide:

$$As_2O_3 + 6HCl \rightarrow 2AsCl_3 + 3H_2O \qquad (5.23)$$

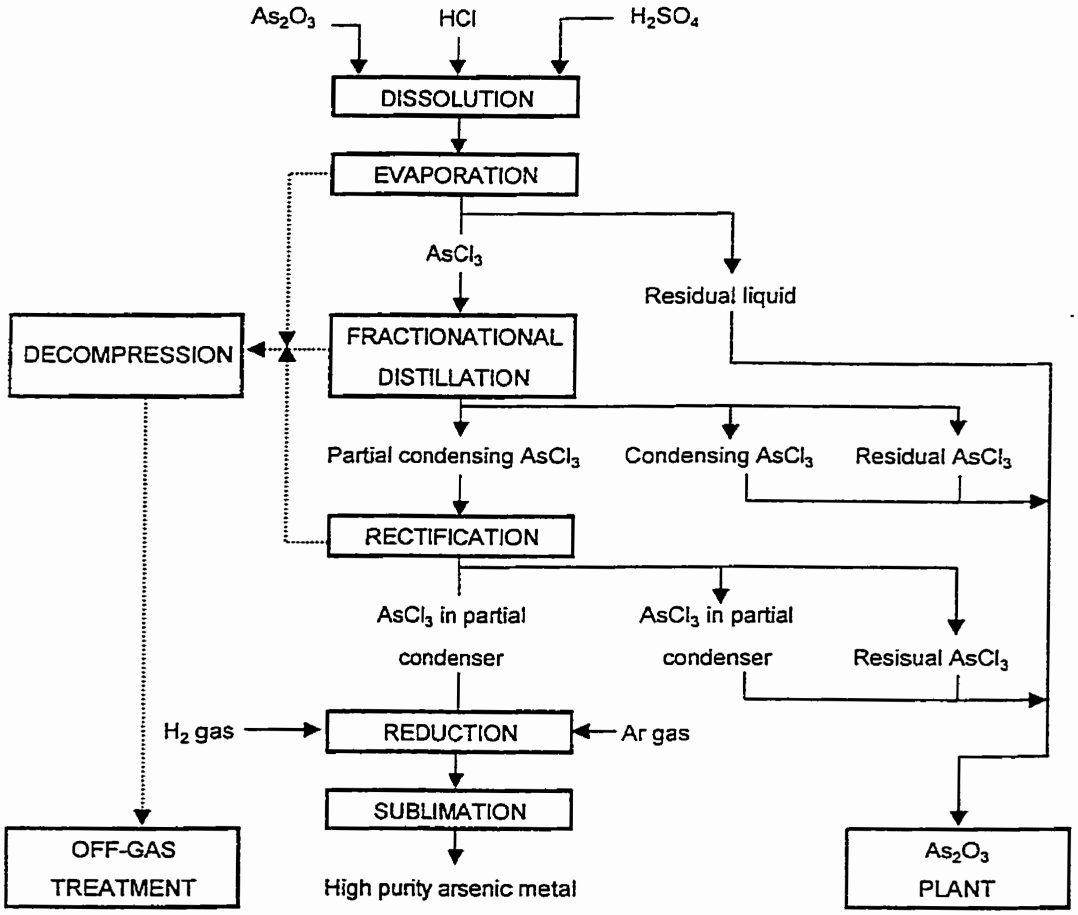


Figure 5.7. Production of arsenic metal at Sumitomo Metal Mining Co. (Toyabe, et al., 1988)

$AsCl_3$ is then evaporated below 100°C using a reflux condenser. Refined $AsCl_3$ is then obtained by fractional distillation to eliminate higher vapor pressure chlorides, such as Si and Ge. It is then reduced with pure hydrogen to produce high purity arsenic metal by cooling the arsenic vapor at 100°C.

$$2AsCl_3 + 3H_2 \rightarrow 2As + 6HCl \tag{5.24}$$

Industrial Minera Mexico Company in México also recovers arsenic trioxide from smelter copper dusts. The arsenic-containing dusts are captured using condensing chambers then fed in a sublimation furnace to obtain purified arsenic trioxide (Sández, 2000).

- **Copper Arsenate Processes**

Development of copper arsenate processes has also been reported. Vircikova and Imriš (1995) reported a process consisting of selective leaching of arsenic from the flue dust in sodium sulfide solution then precipitation using copper sulfate. Arsenic can be removed in the form of a marketable product, e.g., copper arsenate for wood preservation. This process was developed in a laboratory-scale study at the Technical University, Košice in Slovakia for processing of the flue dust from the Krompachy copper smelter. Sodium sulfide solution of 130 g/L, was used as a leaching agent in a stirred reactor at 80 °C for three hours and solid/liquid radio, 1:6. After solid/liquid separation the sulfo-salt solution containing $As_3S_6^{3-}$ was treated by precipitation method using copper sulfate:

$$3AsO_2^- + 6S^{2-} + 6H_2O \rightarrow As_3S_6^{3-} + 12OH^- \tag{5.25}$$

The treatment of the sulfo-salt solution involves the following main step (Figure 5.8):

- Oxidation of As(III) to As(V) by hydrogen peroxide.
- Addition of the mixture of copper sulfate and sulfuric acid to adjust the Cu/As ratio at 1.3.
- Neutralization and pH adjustment by sodium hydroxide

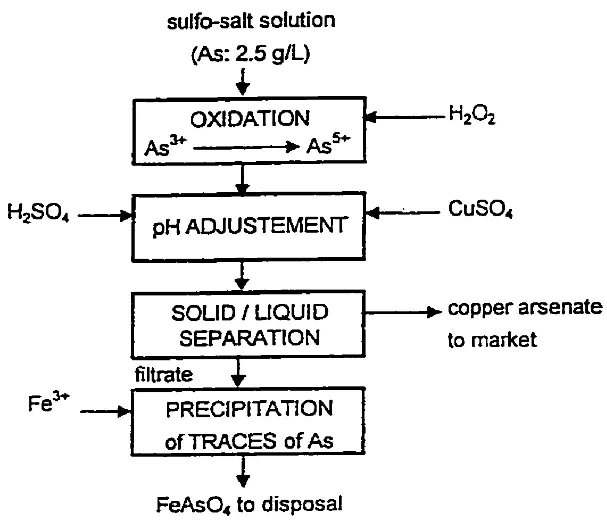


Figure 5.8. Recovery of copper arsenate from sulfo-salt solution.

Stewart, et al. (1995) leached a copper/arsenic sulfide precipitate with oxygen and sulfuric acid at room temperature, producing a crude copper arsenate precipitate, elemental sulfur, and a copper- and nickel-containing solution. The crude copper arsenate was then precipitated as crystalline copper arsenate by the addition of sodium carbonate. Dissolved copper was recovered using metallic nickel and elemental sulfur to produce a precipitate (low-arsenic) suitable for standard nickel-copper processing (Figure 5.9)

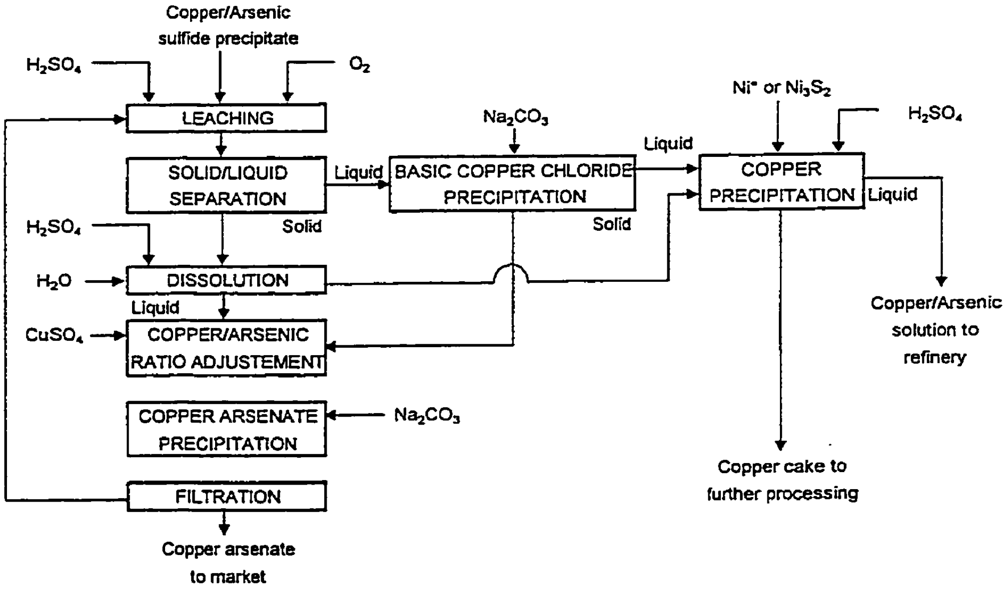


Figure 5.9. Inco's copper arsenate process (after Stewart, et al., 1995)

5.4 From Cobalt Concentrate

Recovery of arsenic from cobalt arsenide concentrate is practiced at Omnium Nord Africain (ONA) in Morroco by roasting. Arsenic trioxide production is 4,500 t/y; however, more data about this operation is not yet available.

CHAPTER VI

ARSENIC DISPOSAL FROM METALLURGICAL PROCESSES

When arsenic is not recovered it is removed from arsenic-bearing residues and stabilized in the form of a solid compound prior to disposal as calcium arsenate, arsenic sulfide or ferric arsenate.

6.1 From Copper Concentrates

6.1.1 Hydrometallurgical Processes

- **Lepanto Mining Company**

A process utilizing sodium sulfide leaching has been proposed by Nadkarni and Kusik (1988), for treating an enargite concentrate at Lepanto Mining Company in Philippines. A typical analysis of the concentrate is shown in Table 6.1. Leaching is accomplished by feeding an excess of Na_2S in 0.25 molar NaOH at 80-105°C. The resulting slurry is filtered to separate the arsenic-free concentrate and recover the leach solution (Figure 6.1) from which sodium thioarsenate is crystallized out by evaporation, cooling and then filtering. The crystals are then treated with sulfuric acid to get arsenic pentasulfide for disposal (reaction 6.1). However, Lepanto Mining Company closed its plant in 1997 due to the exhaustion of its copper concentrate and a planned shift from copper to gold production (Lyday, 1998).

$$2AsS_4^{3-} + 6H^+ \rightarrow 3H_2S + As_2S_5 \qquad (6.1)$$

Table 6.1. Typical chemical analysis of Lepanto's high arsenic concentrate (dry basis)

	Cu, %	As, %	Sb, %	Ag, oz/t	Au, oz/t	Fe, %	SiO_2, %	S, %
Typical analysis	27-30	11-13	0.8-1	5	1.6	9-12	4-5	35

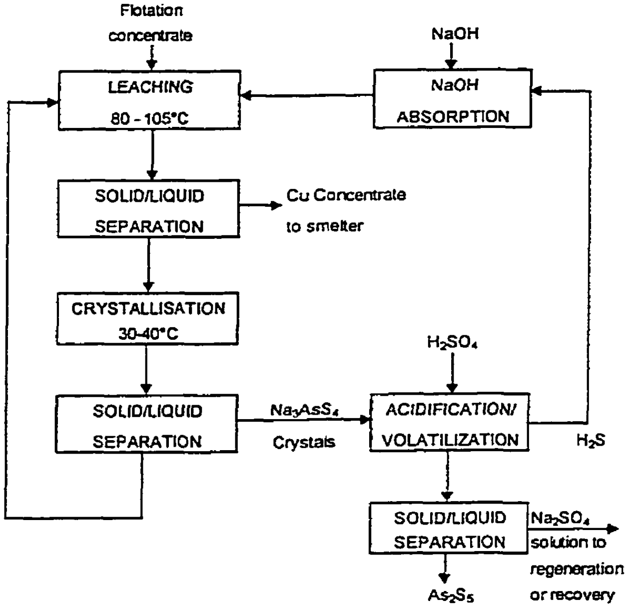


Figure 6.1. Na_2S-preleaching process of Lepanto Mining Company (after Nadkarni and Kusik, 1988)

6.1.2 Pyrometallurgical Processes

Pyrometallurgical processes that remove arsenic from sulfide concentrates have been practiced for many years. Usually, they are based on fluid-bed roasting in a controlled atmosphere to volatilize the arsenic as sulfide and trivalent oxide.

- **Roasting**

In the past the copper concentrate used to be roasted in multiple-bed furnaces. The process was controlled in such a way that optimal conditions for removal of the arsenic prevailed in the upper hearths, whereas in the lower hearths the sulfur content of the material being roasted was reduced to the level required for the subsequent smelting of low-grade matte, e.g., to 15-20% Cu. Roasting is exothermic, and the temperature reaches 500-800 °C. (Grossman, et al., 1997).

After the hot roasting gas had been cleaned in cyclones and dust-settling chambers, operating at approximately 350°C, relatively small quantities of crude arsenic heavily contaminated by flue dust and volatile substances were obtained by cooling the off-gas to below 80°C, in spray coolers or heat exchangers. The As_2O_3 content of the product was generally between 10 and 50%. However, far higher contents can be obtained by using electric precipitators to remove dust from the hot gas. The dust left after cleaning of the hot gas can be processed in a separated process if contains high metal contents.

The cleaned SO_2 - containing gas still contains traces of arsenic and other impurities that have to be removed by washing with water or a circulating washing liquid containing sulfuric acid and by final cleaning in a wet electric precipitator. The sulfur dioxide is used to produce sulfuric acid. The arsenic-containing slurries that accumulate during wet cleaning and effluent treatment are collected, neutralized, and filtered to dispose of arsenic and to recover metals from solution.

In a process developed by Outokumpu, pre-treatment of concentrates is carried out in a rotary kiln at 750 °C under a sulfur vapor atmosphere. Elimination of arsenic and antimony is claimed to be 100% and 50-60%, respectively. Bismuth removal, however, is poor (20-30%) (Piret, 1994).

- **Roasting – Reduction**

An integrated process is proposed by researchers at the Department of Metallurgical Engineering University of Concepción to treat high-arsenic copper concentrates such as the concentrates from Codelco's MM mine and El Indio mine (Padilla, et al., 1998). Arsenic is present in these concentrates mainly as enargite (Cu_3AsS_4) which decomposes readily at high temperatures forming volatile sulfides or oxides depending upon the composition of the atmosphere. The reaction in neutral or reducing atmosphere can be represented by:

$$2Cu_3AsS_4 \rightarrow 3Cu_2S + As_2S_3(g) + S_2(g) \tag{6.2}$$

$$Cu_3AsS_4 + O_2 \rightarrow 3/2\ Cu_2S + \tfrac{1}{2}\ As_2S_3\ (g) + SO_2\ (g) \tag{6.3}$$

In this process, the concentrate is first fed to a fluidized bed reactor, operating between 550-570 °C under neutral atmosphere. The arsenic is volatilized mainly as As_2S_3. The calcine continuously overflows to a second fluidized bed reactor, operating between 800-950 °C and under oxidizing atmosphere, where the remaining sulfur is oxidized, the metal sulfides are oxidized to oxides, and copper ferrites are formed.

The calcine obtained is reduced in a flash-type reactor, where the calcine particles mixed with coal are blown vertically. The partially reduced calcine is further reduced in a molten bath at 1250-1350 °C. Reducing conditions are maintained in the bath by blowing oil or coal directly into the melt. The metallic phase will dissolve the precious metals. Therefore, the metallic copper (black copper) obtained could be electrorefined. This technology could not be accepted by industry because of the numerous steps involved that are not commonly adopted.

Another project which is being tested for Chilean copper concentrates from Chuquicamata, MM and El Teniente mine, and copper – gold concentrates from El Indio mine considers a first step of desarsenifying and dead roast of the concentrate, followed by a carbon reduction of the oxidized calcines in a molten bath. All steps have been investigated in laboratory scale. The neutral roast is being developed at small pilot scale in a double wall-fluid bed reactor (Parada, et al., 1998).

In neutral or reducing conditions, enargite decomposes generating gaseous arsenic sulfide above 500 °C:

$Cu_3AsS_4 \rightarrow 1.5\ Cu_2S + \frac{1}{2}\ As_2S_{3\,(g)} + \frac{1}{2}\ S_2$ (6.4)

Arsenopyrite, also decomposes above 500 – 550 °C generating gaseous As_2S_3 and elemental sulfur. When an inert atmosphere is used, desarsenification can be as high as 95% leaving a calcine still high enough in sulfur to be smelted to matte, or could be dead – roasted followed by carbon reduction in a molten phase. The neutral roasting of high arsenic copper concentrates shows that up to 98% of arsenic removal can be obtained at 650 °C in less than 15 minutes and up to 60% of antimony removal. Condensed product contains 28-46% arsenic.

6.2 From Gold Concentrates

6.2.1 Roasting

Roasting processes have been applied for many years for the treatment of refractory gold ores (e.g., Giant Yellowknife Mines, Campbell Red Lake Mines) (Gagan, 1979). A two-stage roasting process is normally used (Figure 6.2). Kanowna Belle gold mine in Wastern Australia uses a two-stage roasting to remove arsenic from its flotation concentrate and gold recovery by cyanide process (Net Resources Int., 2000).

In the first stage, arsenopyrite is roasted at lower temperature and oxygen deficiency to produce arsenic and avoid the formation of $FeAsO_4$ (Prasad, et al., 1991):

$FeAsS \rightarrow FeS + As\ (g)$ (6.5)

$As\ (g) + 3/2O_2 \rightarrow As_2O_3$ (6.6)

The second stage roast is at a higher temperature with excess oxygen to produce Fe_2O_3 and complete conversion of the sulfides to oxides:

$As_2O_3 + O_2 \rightarrow As_2O_5$ (6.7)

$Fe_2O_3 + As_2O_5 \rightarrow 2FeAsO_4$ (6.8)

$4FeS_2 + 11O_2 \rightarrow 2Fe_3O_4 + 8SO_2$ (6.9)

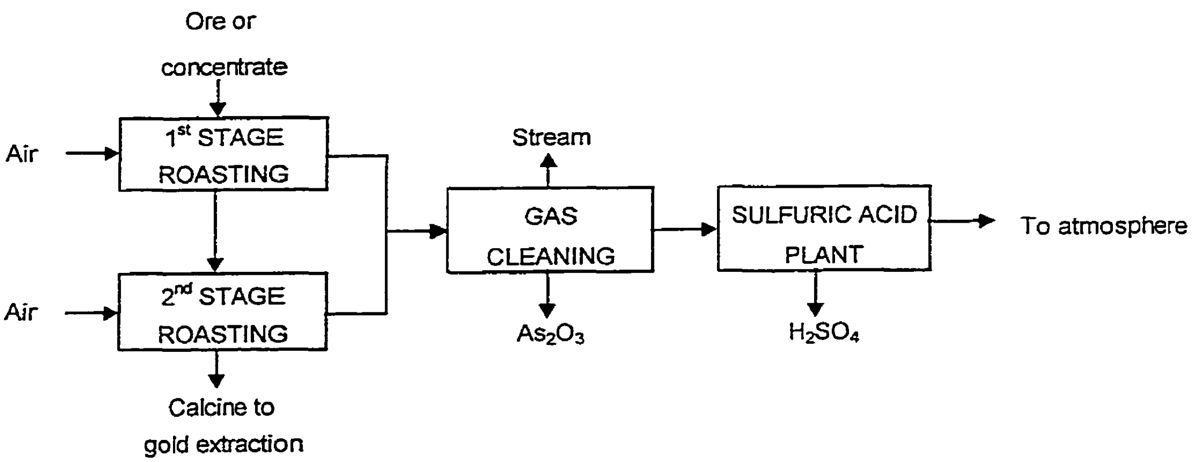


Figure 6.2. Two-stage roasting process (after Kontopoulos and Adam, 1992)

From the environmental point of view, roasting is associated with a number of problems:

- Sulfuric acid production from SO_2 is feasible under special conditions where the concentration of SO_2 in emissions is high. However, many of the refractory gold ores do not meet this special condition.

- The removal of SO_2 is effected by use of lime scrubbing of effluent gases in which up to 95% of the SO_2 is removed. The major disadvantage of this process is the disposal of gypsum

- However, in the case that As_2O_3 produced cannot be marketed, a significant extra cost will occur for its transformation to stable compounds (i.e., ferric arsenate), and a large volume of solid residues will be produced and will have to be disposed of.

Alternative commercially viable methods of oxidation have been developed to eliminate the problems associated with roasting, which are discussed below.

6.2.2 Hydrometallurgical Processes

In refractory auriferous arsenical pyrite concentrates gold is locked within the sulfide minerals and it does not respond to cyanide leaching. An oxidizing pre-treatment step is usually required for an effective breakdown of the sulfide minerals and gold liberation. A number of processes have been presented by Kontopoulos and Stefanakis (1990). Among the hydrometallurgical routes, two processes have found industrial application:

- **Bacterial Oxidation**

The process is based on the aqueous oxidation of pyritic gold ores or concentrates by the action of the bacteria *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* under mild conditions (pH 1-2, temperature 40-55 °C) in agitated reactors. The rate of reaction is low; Complete oxidation of a 40% sulfide concentrate requires 5-7 days (Kontopoulos and Adam, 1992). Arsenic, in the feed is converted to ferric arsenate at the neutralization stage, resulting in a large quantity of low bulk density solid residues that have to be disposed of. The process is practiced commercially in various plants (Table 6.2). These plants, with the exception of Youanmi, use Gencor's BIOX process that employs mixed cultures of *Thiobacillus* and *Lepsospirillum* at 40 - 45 °C. Youanmi employs BacTech (Australia) thermophile bacterial culture that operates at 45 - 55°C (Brierley, 1995). The operation of Ashanti Goldfields at Obuasi in Ghana is the world's largest BIOX facility, and it has treated 2.67 million tons of ore grading 5 g/t gold in 1996 (Coakley, 1997).

Table 6.2. Commercial refractory gold concentrate bacterial oxidation plants (Brierley, 1995)

Plant	Capacity mt/d	Operating History
Fairview, South Africa	35	1986 – present
Harbour Lights, Australia	40	1992 – 1994
Wiluna, Australia	115	1993 – present
Ashanti Goldfields, Ghana	720	1994 – present
Youanmi, Australia	120	1994 - present

- **Alkaline Leaching**

Rossovsky (1993) proposed alkaline leaching for refractory gold concentrates containing pyrite and arsenopyrite. The concentrate was ground to minus 40 μm and decomposed with 200 kg/t NaOH for three hours in a 1.5L flotation machine at 65°C. The pH after decomposition ranged from 8.5-9.5. The leached pulp was then floated, then finely ground to less than 10 μm, and recycled to the leaching circuit together with fresh feed (Figure 6.3). Flotation tailings were then treated with cyanided for three hours using 0.1% cyanide solution. Gold and silver recoveries were 98% and 97%, respectively.

After decomposition, the solid phase contains 0.9-1.5% As and 0.8-2.0% S while the liquid phase contains 10-15 g/L As and 5-7 g/L S. Analysis of the liquid phase after decomposition shows the presence of $S_2O_3^{2-}$ and AsS_3^{3-}. The following reactions are therefore presumed to take place with subsequent oxidation of $S_2O_3^{2-}$ and AsS_3^{3-} to SO_4^{2-} and AsO_4^{3-}, respectively.

$$3FeAsS + 9OH^- + 4O_2 \rightarrow AsS_3^{3-} + 2AsO_4^{3-} + 3Fe(OH)_3 \qquad (6.10)$$

$$FeAsS + FeS_2 + 3OH^- + \tfrac{3}{4}O_2 + 1.5H_2O \rightarrow AsS_3^{3-} + 2Fe(OH)_3 \qquad (6.11)$$

$$FeS_2 + 2OH^- + 1.5O_2 \rightarrow S_2O_3^{2-} + Fe(OH)_2 \qquad (6.12)$$

This process has many potential advantages compared with existing ones, e.g., only a small fraction of the concentrate needs to be reground, low consumption of alkali compared with pressure leaching, and that the process does not allow undecomposed sulfides to pass to cyanidation. Preliminary studies indicate that the treatment cost will be about 80% of that of the roasting-cyanidation process.

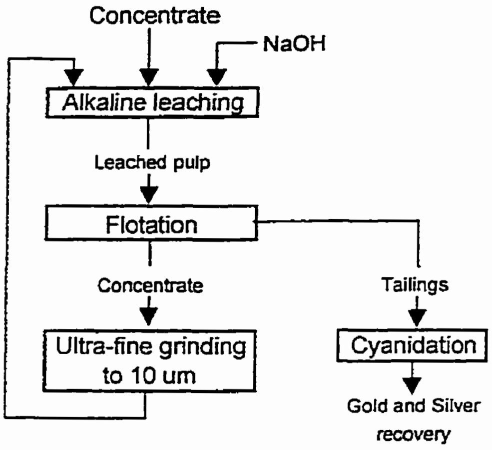


Figure 6.3. Alkaline leaching for refractory gold concentrate

- **High-pressure Aqueous Oxidation**

This process is used at Placer Dome Canada's (PDC) Campbell Gold Mine (Frostiak, et al., 1990), Homestake's MacLaughlin plant, California, São Bento Mineracao, Brazil, The Olimpias Mine in Northern Greece, and the Porgera Complex, Papua, New Guinea (Kontopoulos and Stefanakis, 1989). Leaching is carried out at 170-225°C with total pressures of 1,100-3,200 kPa and oxygen partial pressures of 350-700 kPa and achieves essentially complete oxidation of the sulfides and liberation of the gold within one to three hours. The pressure oxidation can be carried out in either an acid or alkaline medium; the acid medium is preferable because of its lower cost (Berezowsky, et al., 1991). The major reactions are (Kontopoulos and Adam, 1992):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4H^+ + 4SO_4^{2-} \qquad (6.13)$$

$$4FeAsS + 13O_2 + 6H_2O \rightarrow 4H_3AsO_4 + 4Fe^{2+} + 4SO_4^{2-} \qquad (6.14)$$

$$2Fe^{2+} + 0.5O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \qquad (6.15)$$

Other reactions involve oxidation by the Fe^{3+}:

$$FeS_2 + 2Fe^{3+} \rightarrow 3Fe^{2+} + 2S^{\circ} \quad (6.16)$$

$$2FeAsS + 2Fe^{3+} + 4H_2O + 6O_2 \rightarrow 2H_3AsO_4 + 4Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (6.17)$$

Hydrolysis and precipitation reactions occur in parallel:

$$2H_3AsO_4 + 2Fe^{3+} \rightarrow 2FeAsO_4 + 6H^+ \quad (6.18)$$

$$2Fe^{3+} + 2SO_4^{2-} + 2H_2O \rightarrow 2Fe(OH)SO_4 + 2H^+ \quad (6.19)$$

$$6Fe^{3+} + 4SO_4^{2-} + 11H_2O \rightarrow 2(H_3O)\cdot Fe_3(SO_4)_2(OH)_6 + 10H^+ \quad (6.20)$$

The degree of arsenic and iron precipitation and the nature and composition of the precipitated species depend on temperature, acid concentration, sulfate concentration, pulp density, composition and grade of the sulfides, and the nature and quantity of gangue components. Generally, 80 to 98% of the arsenic and 60 to 95% of the iron are precipitated during autoclaving. The solid residue contains the liberated gold, and is treated by conventional cyanidation. The sulfur and arsenic in the feed are ultimately converted to gypsum and ferric arsenate, respectively, requiring high limestone consumption and resulting in a voluminous low bulk-density material that has to be disposed of (Berozowsky, et al., 1991). The residue is characterized as non-toxic and if proper precautions are taken for its safe disposal, it should be of no environmental concern.

The bacterial oxidation is designed to operate as a pre-oxidation step for a portion of the concentrate prior to its introduction into the autoclave. A target of 20% of the concentrate is fed to the bacterial circuit, which accomplishes roughly 50% oxidation of the material with a 1.8 day retention time, facilitating the oxidation of the "easy to oxidize" portion of the concentrate, such as arsenopyrite and carbonaceous minerals. Acid generation of the biological system maintains solution pH, with little need for adjustment, in the range of pH 0.5-1.5 depending on the dominant mineral in the concentrate at the time.

The process flowsheet for Eldorado's São Bento for both oxide and sulfide ore is shown in Figure 6.4.

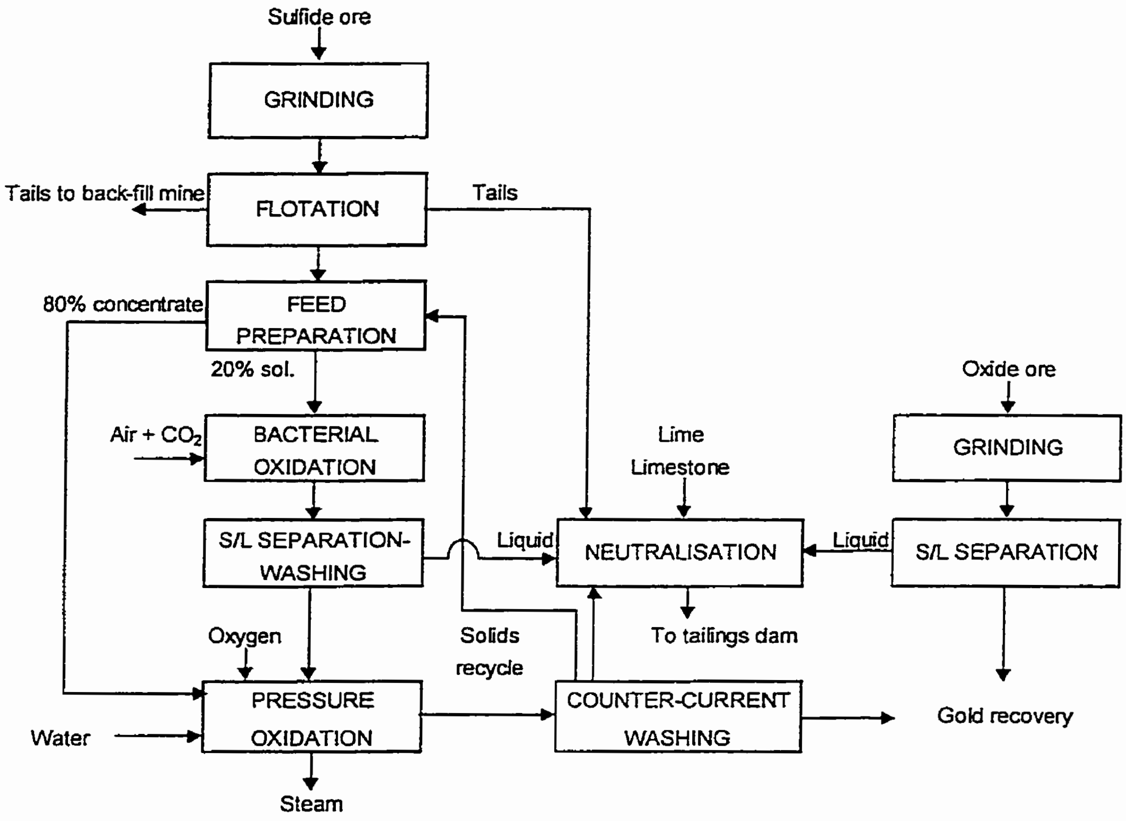


Figure 6.4. Simplified São Bento gold plant process flowsheet (after Shuey, 1998)

The bacterial oxidation stream, after thickening and washing, is recombined with the remaining untreated 80% of the concentrate stream prior to autoclave oxidation at 1,700 kPa, which has a capacity of 150 mt/d, obtaining a sulfur oxidation capacity of 2.5 mt/hr. Following complete oxidation in the autoclave, the concentrate is treated conventionally via CIL, and electrowinning (Shuey, 1998).

6.3 From Copper Smelter Dusts

Several investigations have been carried out to develop a process for disposal of arsenic-containing copper smelter dusts. However, few processes have been applied on a large scale.

- **Selective Leaching with Sodium Sulfide Solution then Precipitation**

Vircikova and Imriš (1995) proposed a selective leaching of high arsenic-containing converter dust using sodium sulfide solution then precipitation using various agents: zinc sulfate, mixture of phosphoric acid with calcium hydroxide, calcium oxide and ferrous or ferric sulfate. In principle, arsenic can be removed as stable precipitate suitable for safe landfill disposal. This process was studied on a laboratory-scale at the Technical University of Košice in Slovakia for the processing of flue dust from the Krompachy copper smelter. Table 6.3 shows an average composition of the dust. Arsenic in dust is present in the form of arsenates (70.6%) and about 15% is in the form of oxides, probably as As_2O_3 (Vircikova and Havlik, 1999).

Table 6.3. The average composition of the flue dust

	%
As	2.38
Bi	2.79
Zn	8.89
Pb	28.0
Sn	12.04
Fe	1.20
Cu	5.27
Sb	3.08
S	6.09

A sodium sulfide solution of 130 g/L, was used as a leaching agent in a stirred reactor at 80 °C for three hours and solid/liquid ratio of 1:6, producing a solution containing $As_3S_6^{3-}$ and AsS^{2-}:

$$3AsO_2^- + 6S^{2-} + 6H_2O \rightarrow As_3S_6^{3-} + 12OH^- \qquad (6.21)$$

Under these conditions, 99.9% arsenic, 4.7% tin, and 6.6% antimony are solubilized while bismuth, zinc, lead, and copper remain in the residue (Vircikova and Imriš, 1995; Vircikova and Havlik, 1999). Three products can be obtained:

1. A mixture of arsenic and zinc sulfide, by using a zinc sulfate solution which is a by-product of the smelter (Fig 6.5). The authors suppose the following reaction:

   $$2As_3S_6^{3-} + 4Zn^{2+} + 2OH^- \rightarrow 3As_2S_3 + 3ZnS + Zn(OH)_2 \qquad (6.22)$$

   This process appears to be feasible, however it uses zinc, which is an expensive reagent and also generates several unstable compounds.

2. An insoluble mixture of hydroxyapatite and calcium arsenate, by the addition of calcium hydroxide in the presence of phosphate ions. The reason for the formation of the arsenate is oxidation of As (III) to As (V) by H_2O_2.

3. A calcium arsenate precipitate, by the addition of calcium oxide after the oxidation of Arsenic (III) and neutralization by sulfuric acid to the pH 2. The efficiency of arsenic removal is over 99%. However, to remove the residual level to ppm, precipitation by Fe (II) or Fe (III) – ions had to be carried out.

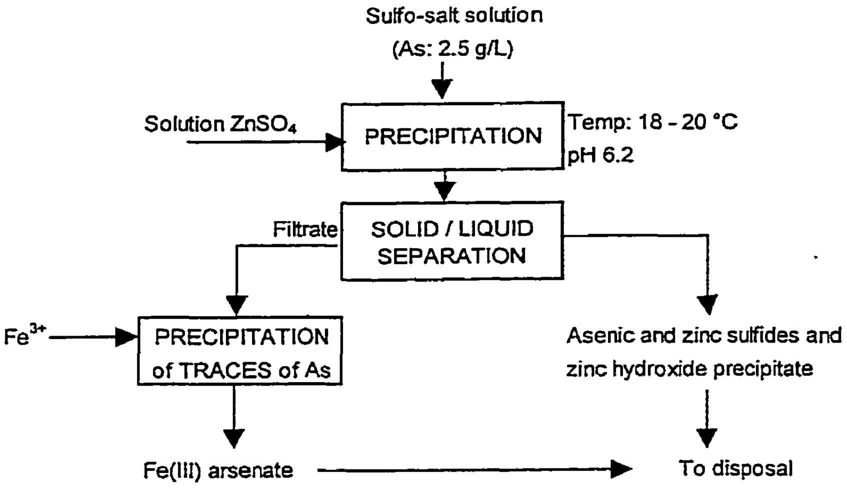


Figure 6.5. Treatment of the sulfo-salt solution by zinc sulfate (Vircikova and Imriš, 1995)

Harris and Monette (1985) also proposed the leaching of Cottrell dust collected at the Horne Copper Smelter by the spent electrolyte from the zinc plant. After the recovery of Zn, Pb, Cd, and Ag, arsenic is disposed in the form of a ferric arsenate/gypsum sludge.

• The Cashman Process

The Cashman process was developed for the high-arsenic ore from the Apex mine in the Cascade mountains east of Seattle (Kunter, 1993). In this process (Figure 6.6), a mixture of finely ground arsenic-bearing ore, concentrate, or flue dust slurry is aerated with recycle calcium chloride brine, sulfuric acid, and a source of iron (if sufficient iron is not contained in the waste) under pressure of 280 to 350 kPa at 120 °C in a titanium reactor. Calcium chloride is used so that the base metals are dissolved as chlorine complexes. The reaction requires from 15 min to 2 hr, depending on the complexity of the material. Arsenic for disposal is precipitated as ferric or calcium arsenate. The installed capital cost for a 100 tons per day pressure autoclave assuming a typical oxidized flue dust containing 6% arsenic and less than 1% sulfides would be $1.6 million (Kunter and Bedal, 1992).

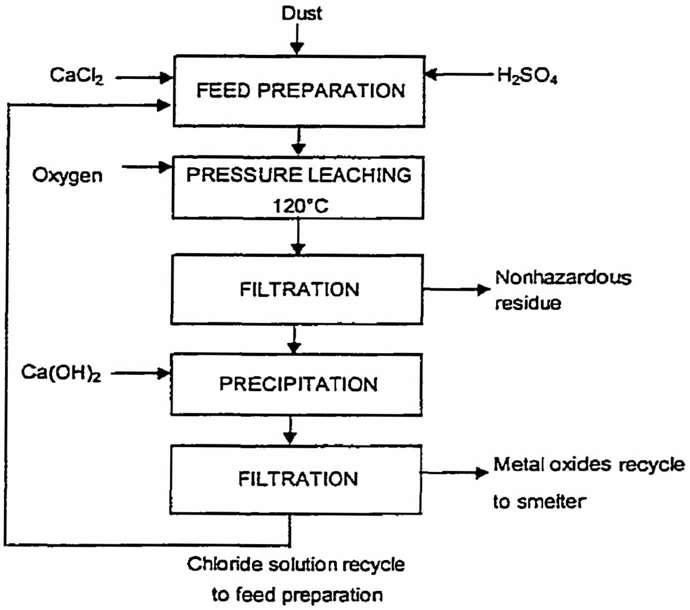


Figure 6.6. The Cashman process flowsheet for an operating smelter (after Kunter, 1993)

Dust leaching under pressure with sulfuric acid and precipitation of arsenic as ferric arsenate has also been investigated by Kennecott (Prater, et al., 1981).

- **Alkaline Dissolution**

Grossman, et al. (1997) described a method for arsenic removal from copper smelter dusts by leaching under pressure at 900 kPa in copper sulfate electrolyte with an additional alkaline leaching step where arsenic is dissolved as Na_3AsO_4 and then crystallized In the case of dusts containing 13.9% Cu, 2.05% Zn, 5.6% Fe, and 9.51% As, about 87% of As stays in the iron-containing residue. All the valuable metals pass into solution.

Figure 6.7 shows a multistage process in which Cu, Cd and Zn are separated off in solution after a neutralization step. Arsenic is precipitated together with lead and the precious metals are dissolved in a further chloride-sulfate leaching step. During a subsequent alkaline leaching step, arsenic is dissolved as Na_3AsO_4 and then crystallized out. By adding iron (III) sulfates, the soluble arsenic constituents are precipitated. An iron arsenate residue suitable for disposal is obtained.

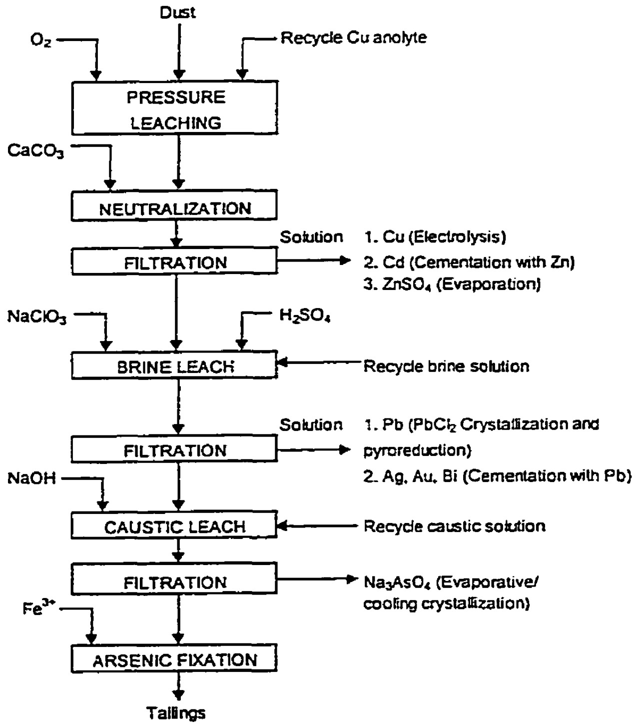


Figure 6.7. Process for recovering metal values from arsenic-containing dusts (after Grossman, et al., 1997).

Sánchez, et al., (1995) also reported results for arsenic removal from Mexicana de Cobre smelter flue dust by alkaline leaching. However, the high concentrations and excessive consumption of NaOH in leaching was restrictive for application of the process.

- **Stabilizing Arsenic Trioxide Flue Dust by Using SMITE**

White and Toor (1996) proposed a process known as SMITE (Synthetic mineral immobilization technology) for arsenic disposal as an apatite-type compound (known as svabite), which is a mineral currently recognized for incorporating arsenic at high concentrations, having the ideal stoichiometry $Ca_5(AsO_4)_3F$. A basic process for stabilizing arsenic is shown in Figure 6.8. Arsenic must be oxidized to the pentavalent state as the trivalent form is more soluble and toxic. Then, either lime or calcium fluoride are added in slight excess to accommodate fluctuations in dust composition. Slacked lime and calcium fluoride are slurried together with the As_2O_3 (arsenolite) at room temperature for periods of 30 minutes to several hours. The reaction is regarded as complete when arsenolite can no longer be detected by X-ray diffraction. During this reaction, a compound (containing water of crystallization) precipitates according to:

$$3As_2O_3 + 9CaO \rightarrow 2Ca_{4.5}(AsO_3)_3 \qquad (6.23)$$

The precipitate is separated by vacuum filtration and the solid containing < 10 % water (the filtrate containing < 5 ppm arsenic is recycled) is dried, then fired in air for 30-60 minutes at 1,000-1,100 °C:

$$2Ca_{4.5}(AsO_3)_3 + CaF_2 + 3O_2 \rightarrow 2Ca_5(AsO_4)_3F \qquad (6.24)$$

The final product approaches theoretical density (3.5 g/cm^3) and contains ≈ 22 % arsenic, which may be disposed of directly or used as aggregate to produce a SMITE concrete. The cement acts as a secondary barrier to dissolution and can be used to pump the waste into landfills.

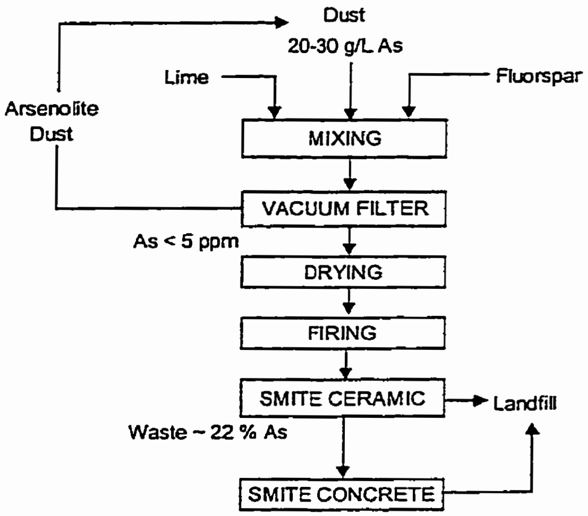


Figure 6.8. Flowsheet of SMITE stabilization of arsenical flue dust (after White and Toor, 1996).

• Aqueous Processing of Arsenic Trioxide to Scorodite

Van Weert and Droppert (1994) described a process where arsenic trioxide was added to a mixture of 2 M nitric acid containing ferric nitrate, and oxidized at 160°C to the pentavalent state precipitating ferric arsenate known as scorodite:

$$As^{3+} + 4H_2O \rightarrow AsO_4^{3-} + 8H^+ + 2e^-$$

$$2NO_3^- + 8H^+ + 6e^- \rightarrow 2NO + 4H_2O$$

overall reaction $$As^{3+} + 2NO_3^- + 8H^+ \rightarrow AsO_4^{3-} + 2NO + 4H_2O \qquad (6.25)$$

Pentavalent arsenic then reacts with Fe^{3+} to precipitate scorodite:

$$Fe^{3+} + AsO_4^{3-} + 2H_2O \rightarrow FeAsO_4 \cdot 2H_2O \qquad (6.26)$$

The resulting NO gas is reconverted to nitric acid in a conventional HNO_3 absorption tower. The mother liquor, with the nitrates, recycles to the absorption tower (Figure 6.9). The process appears to be feasible, but requires an autoclave and a nitric gas absorption plant.

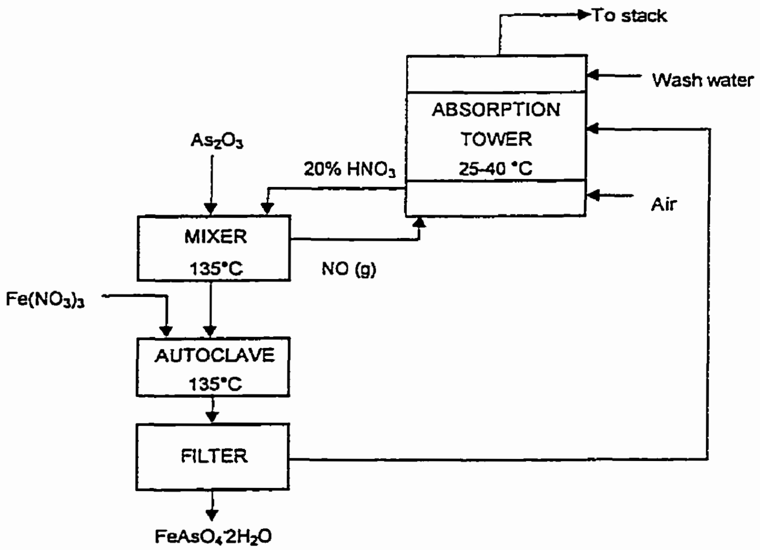


Figure 6.9. Schematic flowsheet for the processing of As_2O_3 to scorodite ($FeAsO_4 \cdot 2H_2O$). (after Van Weert and Droppert, 1994)

- **Japanese Smelters**

Hydrometallugical processes have been implemented at the Saganoseki and Kosaka smelters in Japan to treat the dust generated in their copper smelting operations. The Saganoseki plant was constructed in 1982 and has been operating satisfactorily to remove minor elements from copper smelting (Figure 6.10). 500 t/month of converter dust can be treated in this dust treatment plant where arsenic is fixed as arsenic sulfide, then polymerized and stored in the smelter (Hino, et al., 1995). The hydrometallurgical plant at Kosaka smelter started its operation in 1975 (Mohri and Yamada, 1976). The basic step in the process (Figure 6.11) are leaching of the dust to recover lead sulfate in the residue, copper recovery from the solution, ferric arsenate precipitation as the most stable form for arsenic disposal, cadmium recovery as sponge cadmium and finally zinc recovery as zinc hydroxide from the solution.

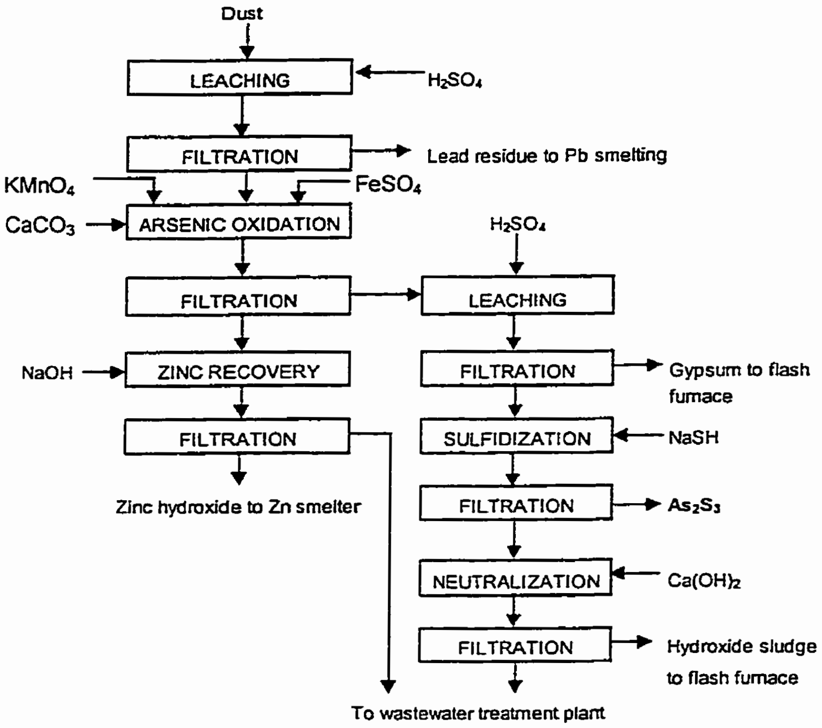


Figure 6.10. Dust treatment plant at Saganoseki smelter (after Hino, et al., 1995)

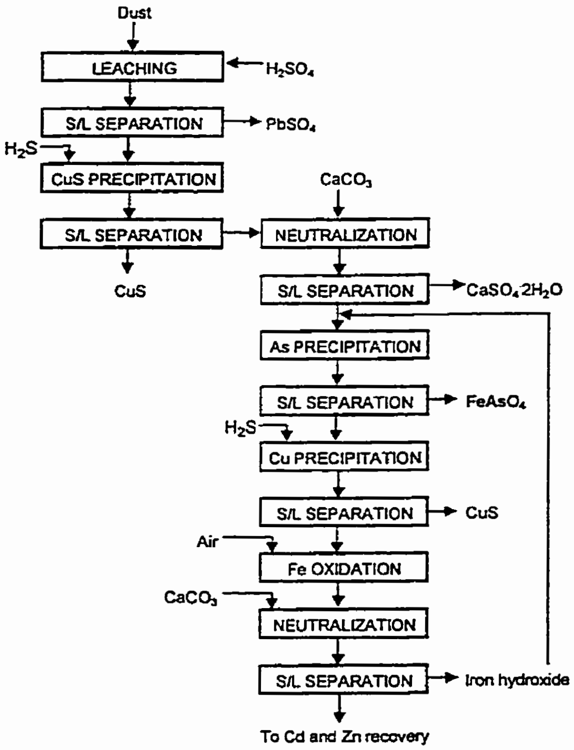


Figure 6.11. Dust treatment plant at Kosaka smelter (after Minoura and Maeda, 1984)

- **Kennecott Hydrometallurgical Process**

The flowsheet of this process is shown in Figure 6.12 (Gabb, et al., 1995). The flash furnace electrostatic precipitator dust (Table 6.4) is water leached and the slurry is pumped to a thickener. The overflow is returned for dust wetting and a bleed is pumped to the copper precipitation stage to maintain solubilised copper at 35 g/L. Thickener underflow is pumped to the acid leaching stage where a sufficient concentration of sulfuric acid is maintained to dissolve the bismuth. It was also determined that chloride ion gave higher extraction rates presumably through the formation of soluble bismuth chloride compounds. Table 6.5 shows typical extractions of elements in water and in H_2SO_4. A thickener is used for liquid/solid separation after acid leaching where overflow is pumped to bismuth precipitation and the underflow is pumped to copper precipitation.

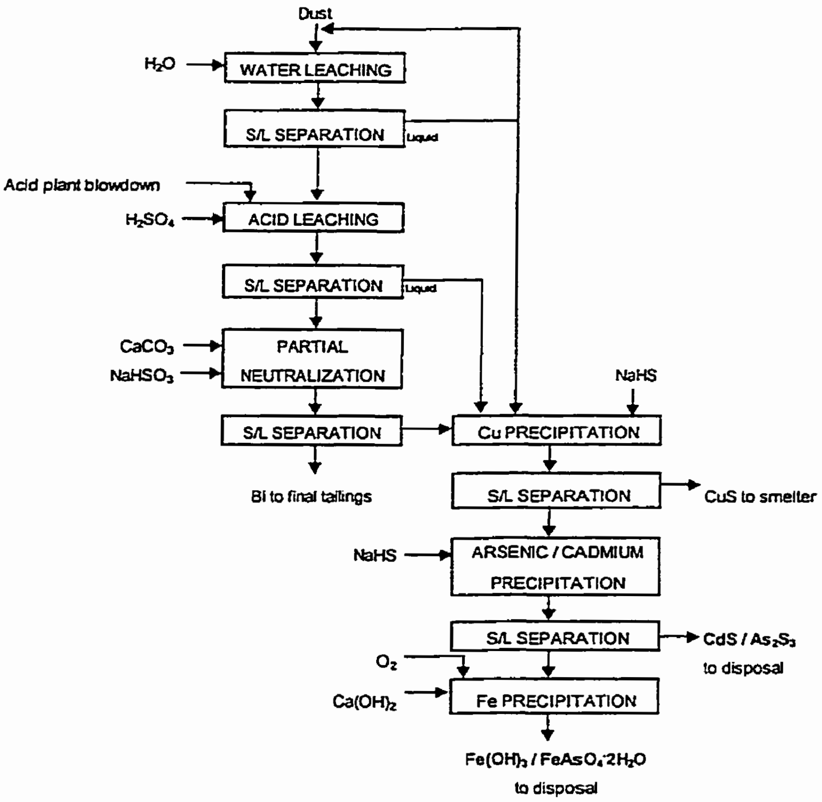


Figure 6.12. Kennecott hydrometallurgical process (after Gabb, et al., 1995)

Table 6.4. Composition of flash furnace dust (wt%)

Element	Average Content	Range
Cu	26	15-30
Pb	1.3	0.50-2.0
As	2.2	0.90-4.2
Sb	0.05	0.03-0.09
Bi	0.20	0.11-0.60
Mo	1.5	0.70-0.30
Zn	1.6	0.80-3.20
Cd	0.05	0.02-0.20

Table 6.5. Water and acid leaching extractions of flash furnace dust (Cumulative basis)

Element	Water leaching % Extracted[1]	Acid leaching % Extracted[2]	Residue % Remaining
Cu	66	8	26
Fe	8	14	78
As	8	75	17
Bi	2	80	18
Zn	45	10	45
Cd	71	7	22

[1] Water leaching extraction at 32°C for 15 minutes.

[2] Acid leaching extraction at 80°C for 30 minutes at initial 150 g/L sulfuric acid, 4 g/L chloride ion and 4 g/L fluoride ion.

Partial neutralization of the acid solution with $CaCO_3$ to a pH of 2.2 is optimum to precipitate the bismuth, but is too high to get a clean separation of iron which also partially precipitates as iron arsenate. The main precipitation reactions are:

$$Bi_2(SO_4)_3 + 2CaCO_3 + 6H_2O \rightarrow Bi_2(OH)_4SO_4 + 2CaSO_4 \cdot 2H_2O + 2CO_2 \qquad (6.27)$$

$$2FeSO_4 + 2CaCO_3 + 3H_2O \rightarrow FeCO_3 \cdot Fe(OH)_2 + 2CaSO_4 \cdot 2H_2O + CO_2 \qquad (6.28)$$

Sulfite ion is also used to reduce iron and arsenic oxides. The degree of reduction is controlled at 180 to 200 mV.

$$2Fe_2(SO_4)_3 + 2NaHSO_3 + 2H_2O \rightarrow 4FeSO_4 + Na_2SO_4 + 3H_2SO_4 \quad (6.29)$$

$$2H_3AsO_4 + 2NaHSO_3 \rightarrow 2HAsO_2 + Na_2SO_4 + H_2SO_4 + 2H_2O \quad (6.30)$$

Copper is then precipitated at pH 2.2 by sodium hydrosulfide (NaHS) and recycled to the smelter.

$$2CuSO_4 + 2HS^- \rightarrow 2CuS + H_2SO_4 + SO_4^{2-} \quad (6.31)$$

Arsenic and cadmium are also precipitated using NaHS. The pH for the arsenic stage is dependent on how much smelter weak acid is added to the stage. Weak acid contains around 100 g/L free sulfuric acid and the plant can precipitate all the arsenic from solutions at this full acid strength. However, if a good cadmium precipitation is required with arsenic, it is necessary to restrict the acid strength passing to the arsenic stage. The lower the acid strength, the better the cadmium precipitation (Gabb and Davies, 1999).

$$2CdSO_4 + 2NaHS \rightarrow 2CdS + H_2SO_4 + Na_2SO_4 \quad (6.32)$$

$$4HAsO_2 + 6NaHS + 6H^+ \rightarrow 2As_2S_3 + 6Na^+ + 8H_2O \quad (6.33)$$

After the preceding stages, a free acid solution remains containing reduced iron and zinc together with minor quantities of cadmium and arsenic. Oxidation of the iron with oxygen and neutralizing to a pH of 2.5 will precipitate a hydrated ferric oxide and ferric arsenate. Finally, slurry at pH of 10 from iron precipitation stage is discharged to the tailings dam.

$$2FeSO_4 + 0.5O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (6.34)$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 + 2H_2O \rightarrow 2Fe(OH)_3 + CaSO_4 \cdot 2H_2O \quad (6.35)$$

$$2HAsO_2 + Fe_2(SO_4)_3 + 3Ca(OH)_2 + 4H_2O \rightarrow 2FeAsO_4 \cdot 2H_2O + 3CaSO_4 \cdot 2H_2O \quad (6.36)$$

Another process is also described by Godbehere, et al. (1995) to treat an arsenic-bearing weak acid effluent and precipitator dust from the Horne Copper Smelter using iron and zinc derived from acid mine drainage and precipitate arsenic as iron and zinc arsenite-arsenates.

6.4 From Cobalt Ores and Concentrates

Considerable research has been performed on arsenical ores and concentrates containing cobalt, resulting in several patents (Ritcey and Ashbrook, 1981). Acid or alkaline leaching in presence of an oxidizing agent has usually been used to treat these ores.

- **Acid Leaching**

This process, known as the Calera process (Figure 6.13), has been applied for the recovery of cobalt from a sulfarsenide ore. Leaching is carried out at 200°C, and under oxygen pressure of about 1200 kPa (Habashi, 1999).

$$CoAsS + 7/2O_2 + H_2O \rightarrow Co^{3+} + SO_4^{2-} + AsO_4^{3-} + 2H^+ \qquad (6.37)$$

$$AsO_4^{3-} + Fe^{3+} \rightarrow FeAsO_4 \qquad (6.38)$$

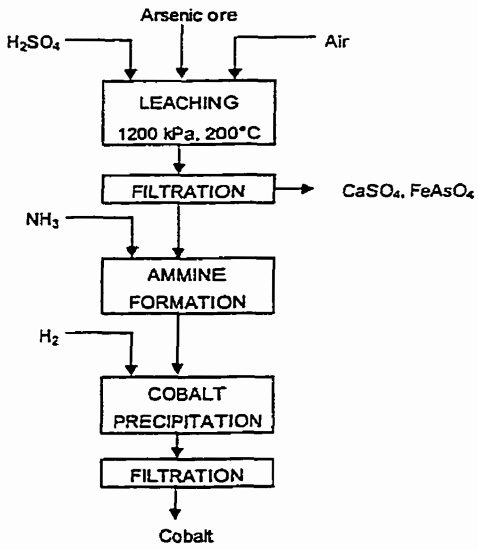


Figure 6.13. Calera process for pressure leaching of arsenical ores (Habashi, 1999)

- **Alkaline Leaching**

Oxidation in presence of NaOH results in solubilizing both arsenic and sulfur and sulfate respectively, while the metal values remain undissolved (Figure 6.14).

$$CoAsS + 7/2O_2 + 5OH^- \rightarrow Co(OH)_3 + SO_4^{2-} + AsO_4^{3-} + H_2O \qquad (6.39)$$

Treatment is carried out at 115°C and 840 kPa oxygen pressure. Arsenic can be removed from the leach solution by precipitation with lime to give calcium arsenate, or with H_2S to give arsenic sulfide. When lime is used, sodium hydroxide is regenerated:

$$2AsO_4^{3-} + 3Ca(OH)_2 \rightarrow Ca_3(AsO_4)_2 + 6OH^- \qquad (6.40)$$

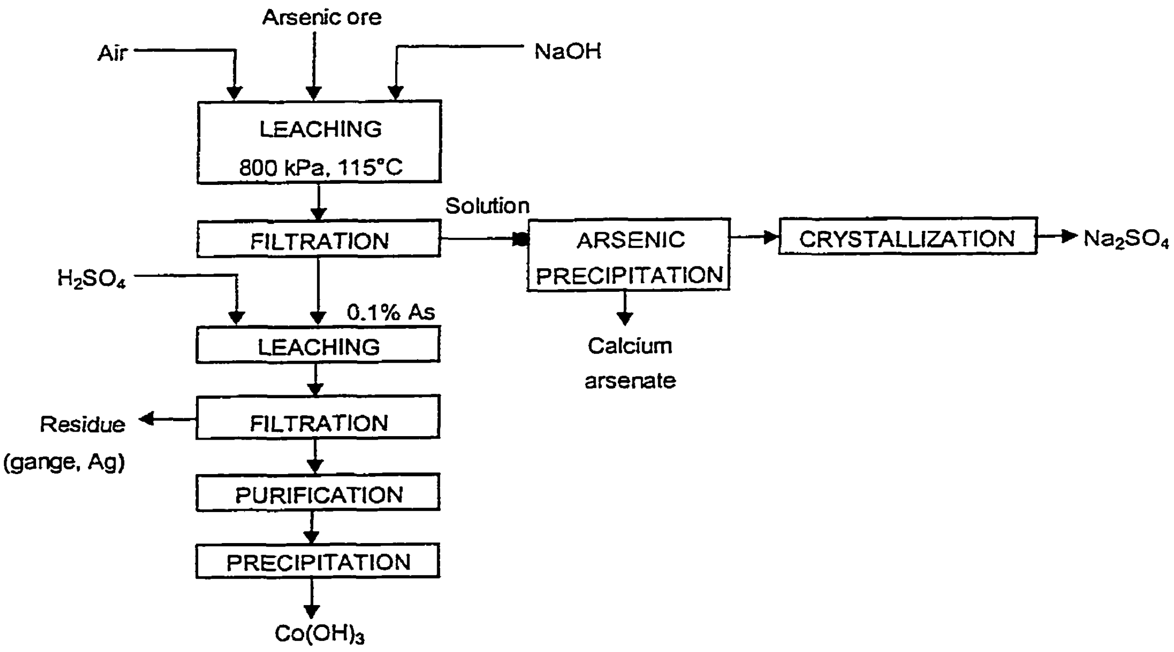


Figure 6.14. Leaching of arsenide ore with sodium hydroxide (Habashi, 1999)

6.5 From Arsenic-containing Solutions

The removal of arsenic from process solutions and effluents has been practiced by the metallurgical industry for many years by the formation of metal arsenites and arsenates as it was shown in section 2.5, although other methods have been investigated and/or used (Harris, 2000; Nishimura, et al., 2000). These include:

- Neutralization with lime to precipitate calcium arsenite/arsenate (Laguitton, 1976; Robins and Tozawa, 1982) followed by calcination to produce a stable product, $Ca_3(AsO_4)_2$, (Nishimura and Tozawa, 1985). Variations of this process are currently operating in Chilean copper smelters as mentioned in section 4.4.1. A flowsheet of this route is shown in Figure 6.15.

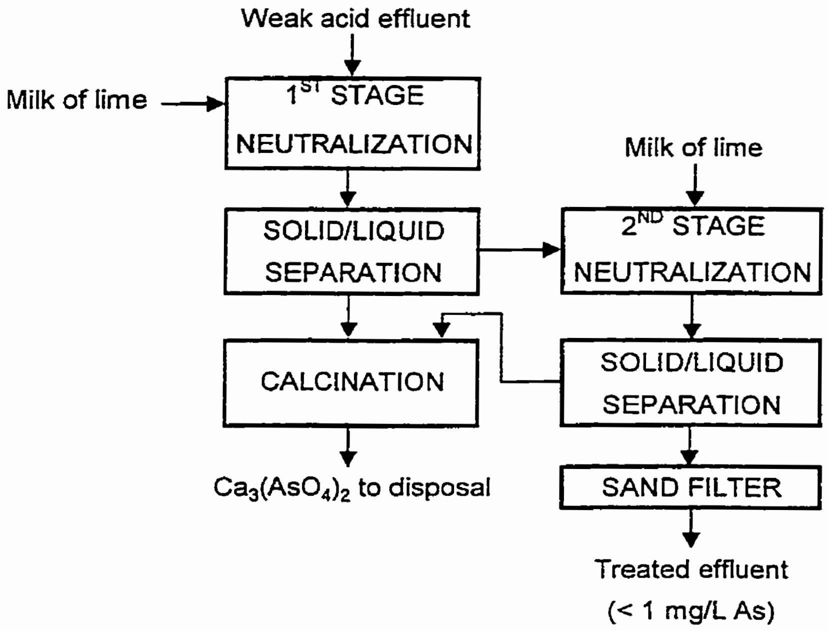


Figure 6.15. Two-stage lime precipitation (after Donnelly and Evans, 2000)

- Neutralization and precipitation as arsenic sulfide, which is either further processed or returned to the smelting process (Donnelly and Evans, 2000). In Japan, at Saganoseki smelter, arsenic is precipitated as arsenic sulfide and then polymerized by an autoclave and stored (Hino, 1995).

- Neutralization and precipitation as ferric arsenite (Stefanakis and Kontopoulos, 1988) and amorphous ferric arsenate at low temperature (Harris and Monette, 1988; Krause and Ettel, 1985; Papassiopi, et al., 1988), which have a molar Fe:As ratio > 4. This process is effective for low arsenic-containing effluent. However for the fixation of arsenic in arsenic-rich solution or flue dust, the application of this method would lead to the generation of a large volume of amorphous arsenic-bearing ferrihydrite/gypsum sludge because of the necessity to attain Fe/As molar ratio > 4 for sale disposal of it.

- Neutralization and precipitation as crystalline ferric arsenate, known in the nature as scorodite, at high temperature (Dutrizac, et al., 1987; Krause and Ettel, 1989; Robins, 1990; Demopoulos et al., 1994; Swash and Monhemius, 1994, 1998; Droppert, 1996; Monhemius and Swash, 1999). This compound does not require a high Fe/As molar ratio in the starting solution and it also has a lower arsenic solubility (typically < 1 ppm As at pH = 5.0).

- There are other metal arsenates, e.g., of Ba^{2+}, Cu^{2+} and Pb^{2+}, which are less soluble and more stable in the neutral pH region than the calcium or ferric arsenates, but these have not been seriously considered as disposal forms (Nishimura, et al., 2000). The insolubility of barium arsenate, $Ba_3(AsO_4)_2$, was the basis of a patent for arsenic removal, but this was shown to be incorrect (Robins, 1985b). Twidwell, et al. (1995) have demonstrated that calcium phosphate arsenate with apatite structure presents low solubility and appropriate stability for disposal. Comba, et al. (1988) have studied in detail the synthesis of the mineral compound mimetite, $Pb_5(AsO_4)_3Cl$, under conditions of ambient temperature and pressure, and found it to be one of the most insoluble arsenic compounds.

Also, a number of other arsenic removal techniques, e.g., ion exchange, solvent extraction, membrane separations, have been investigated and/or actually are in use. Table 6.6 summarizes some of these processes together with some selected references.

Table 6.6. Several methods for arsenic removal from solutions

Separation process	Application	Selected references
Adsorption	- Arsenic (V) adsorption on ferric hydroxide	- Gupta and Chen, 1978; Pierce and Moore, 1982; Leckie, et al., 1985; Robins, et al., 1988
	- Adsorption of As(III) onto ferric hydroxide	Nishimura and Robins, 2000
	- Aluminum hydroxide and carbon	- Nishimura and Umetsu, 2000
	- Other adsorbents have been investigated	- Anderson, et al., 1976; Huang and Fu, 1984; Eguez and Cho, 1987 Accardo, et al., 1995
	- Coprecipitation	- Frost and Griffin; Madsen and Martin, 1983; Xuewen, et al., 1998
		- Liao, 1980; Castro and Muñoz, 2000; Tahija and Huang, 2000
Electrolysis	- Liberator tanks for copper refinery solutions	- Dewalens, et al., 1975; Shibata, et al., 1987; Toyabe, et al., 1987; Baradel, et al., 1986
	- Alkaline electrolysis/ Production of arsenic metal	- Kozmin, et al., 1970; Takagi and Yabe, 1956; Menzies and Owen, 1966
Ion exchange	- Anion exchange investigated and used for As(III) and As(V)	- Nelson and Kraus, 1955; Danielsson, 1965; Kholmanskikh, 1971; Egawa, et al., 1985; Nenov, et al., 1997
Solvent extraction	- Many laboratory investigations	- Gavrichev, et al., 1969; Tserekova, et al., 1970; Totsuka, et al., 1986; Baradel, et al., 1986; Szilassy and Vadasdi, 1990
	- Several plant processes	- Takahashi, et al., 1980; Royston and Hunter, 1983; De Schepper, 1985; O'kane, 1985; Jiaoyong, et al., 1990; Rondas, et al., 1995
Membrane separations	- Precipitate membranes used in laboratory	- Lefebvre and Robins, 1985; Jian, 1998
Precipitate flotation	- Effective for As(V) adsorbed on ferric hydroxide	- Schlicher and Ghosh, 1985
Ion flotation	- Anion flotation	- Clarke and Wilson, 1983; Matis, et al., 1997
Biological processes	- Algae and aquatic plants reported to remove As	- Maeda, et al., 1985; Solozhenkin, et al., 1999
	- Arsenic resistant organisms	- Brown, et al., 1983; Dambies, et al., 1999

CHATER VII

SUMMARY OF ARSENIC TREATMENT PROCESSES

7.1 Arsenic Recovery

Arsenic trioxide, 99.9% As_2O_3, is the main commercial arsenic compound recovered, either by roasting or leaching from gold, copper and cobalt concentrates or copper smelter dusts (Table 7.1 to 7.3):

- Roasting of copper concentrate at the El Indio mine in Chile results to a concentrate having $< 0.1\%$ As, rendering the concentrate more acceptable as smelter feed. Arsenic recovery in the bag house ranges between 80% to 98%.

- Roasting of gold concentrate has been applied to recover arsenic trioxide, principally in Canada. However, due to environmental reasons and to the collapse of the market of As_2O_3 resulted in the shut down of roaster operations and the application of a pressure oxidation process as at Cambell Red Lake Mines Ltd.

- Roasting of cobalt arsenide concentrate is practiced at Omnium Nord Africain (ONA) in Morocco; however, more data about this operation is not yet available.

- The copper arsenate circuit at Equity Silver Mines Limited had good results during its operation. But, new industrial operations have not been reported in the literature.

- Production of arsenic trioxide and arsenic metal at Sumitomo Metal Mining Company in Japan have well performed for many years. However, these operations are not preferable from economical standpoint because the complex composition of the dusts. Also, in the past years, the market for arsenic compounds like arsenic trioxide and arsenic metal have not grown, thus creating a surplus of arsenic production, however they are essential to the copper smelting going on.

Table 7.1 Present arsenic recovery operations from copper and cobalt concentrates

Operation	Copper concentrate	Cobalt concentrate	Copper concentrate
	El Indio mine Chile	**Omnium Nord Africain (ONA) Morocco**	**Equity Silver mine Canada**
Subject	Roasting	Roasting	Leaching
Commodity	As_2O_3	As_2O_3	Copper arsenate
Production, t/y	12,500	4,500	Stopped
As, %	96-97.5	high purity	
Parameters			
Capacity, t/y	110,000	N.A.	33,000
Minerals in the feed	Cu_3AsS_4 $(CuFe)_{12}As_4S_{13}$ $(CuFe)_{12}Sb_4S_{13}$ $Cu_3(Sb,As)S_4$	CoAsS - - -	$CuFe)_{12}As_4S_{13}$ $(CuFe)_{12}Sb_4S_{13}$ FeAsS ZnS, ZnS
As in the feed, %	8.0-8.5	N.A.	4
S in the feed, %	32-36	N.A.	N.A.
Cu in the feed, %	23-25	-	17
Reagent for oxidation	Air, fuel oil	Air, fuel oil	NaHS
Consumption	N.A.	N.A.	N.A.
Temperature, °C	550-750	N.A.	107
Reagent for precipitation	-	-	O_2, $CuSO_4$
Consumption	-	-	N.A.
Temperature, °C	-	-	150
Pressure, kPa	-	-	1,400
Concentrate	Calcined	Calcined	Leached
Production	220	N.A.	N.A.
Cu, %	32-34	N.A.	20-22
As, %	0.05-0.1	N.A.	< 1.5
S, %	23-26	N.A.	N.A.
Reference	Buckingham, et al., 1999	Private Communication from I. Akalay to F. Habashi dated 2000/2/11	Edwards, 1985, 1991

N.A.: Not available

Table 7.2 Arsenic recovery operations from gold concentrates

Operation	**Cochenour Williams Canada**	**Dickenson Canada**	**Campbell Red Lake Canada**	**Giant Yellowknife Canada**	**Kerr Addison Canada**	**Lancefield Wastern Australia**	**New Consort South Africa**
Subject				Roasting			
Commodity	As_2O_3	As_2O_3	As_2O_3	As_2O_3	As_2O_3	As_2O_3	As_2O_3
Production, t/d	N.A.	N.A.	6.3	N.A.	N.A.	N.A.	2.0
As, %	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	94-97
Extraction							
As, %	84	N.A.	81	89	N.A.	N.A.	88
S, %	93	N.A.	93	88	N.A.	N.A.	92
Parameters							
Capacity, t/d	20	12-16	60	130	N.A.	400	100
Stages	1	1	2	2	1	1	2
Minerals in the feed	FeAsS	FeAsS	FeAsS, FeS_2	FeAsS	FeAsS	FeAsS	FeAsS
	FeS_2	FeS_2	Stibinite	FeS_2	FeS_2	FeS_2	FeS_2
		-	Pyrrhotite	Stibinite	-	Pyrrhotite	Pyrrhotite
As in the feed, %	6.3	8	7-9	7-9	1	1.4	2-3
S in the feed, %	18.3	20-36	17-18	20.2	42	24	32-40
Au in the feed, oz/t	N.A.	1-2	0.66	3.82	0.45-0.6	1.73	4.8-7.4
Reagent for oxidation	Air	Air	Air	Air	Air	Air	Air
Consumption, m^3/hr	N.A.	N.A.	N.A.	N.A.	N.A.	14,000	6,000
Temperature, °C	550-750	705-750	590-620	N.A.	370	630-650	640-790
Calcine							
Production, t/d	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	72
As, %	1.3	N.A.	1.0	1.0	N.A.	N.A.	0.3-1.5
S, %	1.6	N.A.	1.6	2.5	N.A.	N.A.	0.4-0.8
Reference	Piret and Melin, 1989; Maycock, et al., 1990	Gagan, 1979	Frostiak and Haugrud, 1995	Piret and Melin, 1989	Gagan, 1979	Brown, et al., 1990	Penman, 1985; Ferreira, et al., 1989

N.A.: Not available

Table 7.3 Present arsenic recovery operations from copper smelter dust

Operation	**Sumitomo Metal Mining, Japan**	
Subject	Leaching	Leaching
Commodity	As_2O_3	Arsenic metal
Production, t/y	720	18
As, %	99.9	99.9999
Parameters		
Capacity, t/y	N.A.	N.A.
Minerals in the feed	As_2S_3	As_2O_3
As in the feed, %	N.A.	99.9
S in the feed, %	N.A.	17 ppm
Cu in the feed, %	N.A.	-
Reagent for oxidation	Air, $CuSO_4$	HCl
Consumption	N.A.	N.A.
Temperature, °C	70	< 100
Reagent for precipitation	SO_2 gas (reduction)	H_2 gas (reduction)
Consumption	N.A.	N.A.
Temperature, °C	N.A.	800-850
Concentrate	CuS	Residual $AsCl_3$
Production	N.A.	N.A.
Cu, %	N.A.	< 0.05 mg/L
S, %	N.A.	< 0.05 mg/L
Reference	Terayama, 1999	Toyabe, et al., 1988

N.A.: Not available

7.2 Arsenic Disposal

Arsenic is removed from refractory gold concentrates or copper smelter dusts by leaching and then precipitated as arsenic sulfide or ferric arsenate prior to disposal (Table 7.4 and 7.5):

- High-pressure aqueous oxidation proved to be an effective method for liberating gold from its refractory ores. Leaching is conduced in autoclaves in acid medium at about 190°C with total pressure of 1,600-2,100 kPa. Arsenic is solubilized and then precipitated as ferric arsenate. Effluent contains < 0.3 mg/L of arsenic.

- Hydrometallurgical processes have been implemented in several copper smelters to treat the dust generated in the process. The basic step is leaching of the dust with H_2SO_4 at 25-130°C to recover Cu, Zn or Pb from the solution, then precipitation of arsenic as ferric arsenate or arsenic sulfide for disposal. Air, H_2O_2, or $KMnO_4$ are used for oxidation of As (III) to As (V) at room temperature. At Kennecott Copper Company in USA, arsenic is reduced to $HAsO_2$ using $NaHSO_3$. In the precipitation stage, arsenic is precipitated with NaHS or $FeSO_4$.

Table 7.4 Present arsenic disposal operations from gold concentrates

Operation	**Campbell Red Lake Canada**	**São Bento Mineracão Brazil**
Subject	Leaching	Leaching
Commodity	Gold	Gold
Production, oz/y	250,000	60,000
Extraction, %		
Direct	< 74	< 40
Oxidized	> 99	> 95
Arsenic compound	$FeAsO_4$	$FeAsO_4$
Extraction, %	N.A.	N.A.
Effluent, mg/L	< 0.3	0.24
Parameters		
Feed		
Capacity, t/d	55-60	700
Mineralogy	FeAsS FeS_2 Pyrrhotite	FeAsS FeS_2 Pyrrhotite
Au, g/t	200-300	25
Fe, %	20	34
As, %	10	9.9
S, %	17-19	18.7
Cu, %	-	-
Reagent	O_2	O_2
Consumption, t/t conc.	0.5-0.6	N.A.
Temperature, °C	195	190
Pressure, kPa	2,100	1,600
	Precipitation	
Reagent	Lime	Lime, limestone
Consumption, t/t conc.	0.8	N.A.
Reference	Bolton and Weir, 1994 Froastiak and Haugrud, 1995	Bolton and Weir, 1994 Da Silva, et al., 1989 Berezowsky, et al., 1988

Table 7.5 Present arsenic disposal operations from copper smelter dust

Operation	**Saganoseki** **Japan**	**Kosaka** **Japan**	**Kennecott** **USA**	**El Teniente[1]** **Chile**	**Chuquicamata[3]** **Chile**
Subject			Leaching		
Commodity	Lead sulfate;	CuS; cement Cu	CuS	CuS	Solution to SX
Production, t/y	Zinc hydroxide 2,520; 1980	4,200; 900	N.A.	42	N.A.
Cu, %	1.2; 9.9	50.4	N.A.	54.4	40–60 g/L
As, %	2.5; 2.2	1; 4.9	N.A.	0.42	8–14 g/L
Compound	As_2S_3	$FeAsO_4$	As_2S_3	$FeAsO_4$	$FeAsO_4$
Extraction, %	61%	85 (leaching)	87	99.65	95.1
Effluent,	41%	0.001 g/L	2.23 g/L	18.3%	7.6 ppm
Parameters					
Feed					
Capacity, t/d	17	2,600	N.A.	8 (20)[2]	100
Mineralogy	$BiAsO_4$, $FeAsO_4$	N.A.	-	As_2O_3	As_2O_3
	$CuSO_4 \cdot H_2O$	-	-	-	-
	$ZnSO_4 \cdot H_2O$,	-	-	-	-
Au, g/t	$PbSO_4$	-	-	-	-
Fe, %	23 (Pb)	12	N.A.	3.8 (total)	11.1
As, %	6	1.3	0.9-4.2	5.7 (total)	5.1
S, %	13 (Zn)	N.A.	N.A.	N.A.	N.A.
Cu, %	5	11.2	15-30	22.4	27.3
Reagent	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Consumption.	40 g/L	90 g/L	150 g/L	30 g/L	0.5-0.6 t/t conc.
Temperature, °C	Room	70-90	80	Room	40-130
			Precipitation		
Reagent					In situ
Oxidation	$KMnO_4$	Air	$NaHSO_3$	H_2O_2	-
Consumption	175, 7.5 kg/t dust	-	(reduction)	12 L/m^3	-
Precipitation	NaHS	-	NaHS	Ferric sulfate	Fe
Consumption, t/t conc.	83 kg/ t dust	-	N.A.	N.A.	-
Reference	Tomita, et al., 1991 Hino, et al., 1995	Mohri and Yamada, 1976; Minoura and Maeda, 1984	Gabb, et al., 1995	Vuskovic, 1996 Araya, 1999	Farias, et al., 1993

[1] Results January-June 1998 ( )[2] Dust processed in 1993 [3] Dust from Outokumpu flash furnace

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS:

Arsenic is a major toxic impurity in the metallurgical industry that is usually found in sulfide ores containing gold, silver, cobalt, nickel, iron, copper, lead and antimony. Release of arsenic compounds originating from human activity can cause substantial environmental contamination because of their toxicity. All arsenic compounds are considerably toxic, especially the inorganic ones, and trivalent compounds are more toxic than pentavalent compounds. Due to the toxicity of arsenic and its compounds, environmental regulators have set very low permissible levels for arsenic in aqueous effluents for the metallurgical industry (0.5-1 mg/L).

Regarding the effects on humans, the International Agency for Research on Cancer determined in 1980 that inorganic compounds are skin and lung (via inhalation) carcinogens in humans. Occupational exposure to inorganic arsenic, especially in mining and copper smelting, has quite consistently been associated with an increased risk of cancer. A number of studies about arsenic poisoning of smelter workers have been reported in the literature. Sulfur dioxide in the smelter environment also seems to play a minor role, if any, in the development of lung cancer.

Regarding the environmental pollution in Canada caused by arsenic in the metallurgical industry, heavy arsenic contamination in three lakes and in a nearby tailing pond have been found near Yellowknife, where about 270,000 tons of arsenic trioxide and 800,000 liters of waste petroleum products were stored underground at an abandoned gold mine during the operation of the Giant mine. The Giant mine was operated by Royal Oak Mines, an American company which was purchased in 1999 by Miramar Mining Corporation, a Canadian company.

Arsenic also adversely affects the copper properties such as castability and rollability, electrical conductivity and workability, such as annealing temperature, hardness, tensile strength, and elongation to failure.

The priority of smelters has been the reduction of impurities emissions into the atmosphere. Sulfur dioxide has been used for sulfuric acid production and arsenic has been mainly recovered as arsenic trioxide, which is eliminated from the copper concentrates principally during the smelting stage by volatilization and slagging. The differences of arsenic elimination processes (smelting/converting) can be explained by the variations in operating conditions at the various smelters, such as feed composition, smelting temperature, converting rate, oxygen enrichment, gas composition, the analysis and relative quantities of products, etc. Trivalent arsenic associated with metallurgical gases is present in vapor form as the dimer As_4O_6. After cooling the gases, arsenic condensation takes place and depending on the arsenic content, condensation starts at a gas temperature of 200°C and is completed at 40-80°C.

The present work has provided an overview of the different processes for recovery or disposal of arsenic from copper, gold, or cobalt concentrates and from arsenic-containing copper smelter dusts or solutions.

Arsenic trioxide, 99.9% As_2O_3, is the main commercial arsenic compound recovered, either by roasting or leaching from gold, copper and cobalt concentrates or copper smelter dusts. The world production of arsenic trioxide has been falling steadily since 1974 because it is a by-product, and production is determined not by the demand for arsenic but by the demand for copper, gold, lead, etc. However, despite environmental regulation that has led to the cessation of production in two large producers: Boliden in Sweden and ASARCO in the United States, new suppliers have emerged to keep the world production, namely China, France, Chile, Ghana, Mexico, Morocco, Namibia, Philippines, and Belgium. However, most countries do not report their arsenic production and world production values have a high degree of uncertainty. In 1998, U.S. Geological Survey estimated the arsenic trioxide production at about 41,000 metric tons. This product is principally used for the production of wood preservatives, where the United States continues to be the world's largest consumer (between 20,000 and 30,000 tons annually). The price for arsenic trioxide imported by the United States is about US$680/mt. The end-use of arsenic in the United States has been about 87% in wood preservatives, 5% in agricultural chemical, 3% in glass manufacturing, 3% as metallic arsenic in nonferrous alloys, and 2% in other uses.

In the past years, the market for arsenical compounds has not grown due to the restrictions of the utilization of arsenic bearing products by environmental regulation. However, the growing use of cellular telephone technology has resulted in a boom for gallium arsenide, a semiconductor material similar to silicon with certain unique properties, such as high frequency operation for microwave circuits and optical properties for fiber optic applications. Many GaAs manufacturers continue to introduce new devices for this market and expand capacity to meet the growing demand, mainly in the United States where in 1997, 22.4 tons of gallium in the form of GaAs were consumed. Commercial-grade arsenic (99% pure) and high-purity arsenic, 99.9999% or greater have been produced.

Roasting operations present an excellent opportunity for recovery of arsenic from copper, cobalt or gold concentrates. However, the selection of operating conditions is critical. The design of the gas cleaning system must provide for collecting the dust carry-over and the volatilized arsenic separately. In some cases, however, sulfuric acid production from SO_2 is not feasible because of its low concentration in the gas. Clean pyrometallurgical processes with an efficient control of atmospheric emissions and efficient removal and disposal processes for the residues could help to solve the problem.

- Roasting of copper concentrate at the El Indio mine in Chile results in a concentrate having < 0.1% As, rendering the concentrate more acceptable as smelter feed. Arsenic recovery in the bag house ranges between 80% to 98%.

- Roasting of gold concentrate has been applied to recover arsenic trioxide, principally in Canada. However, due to environmental reasons and to the collapse of the market of As_2O_3 resulted in the shut down of roaster operations and the application of a pressure oxidation process as at Cambell Red Lake Mines.

- Roasting of cobalt arsenide concentrate is practiced at Omnium Nord Africain (ONA) in Morocco; however, more data about this operation is not available yet.

In hydrometallurgical processes arsenic should be removed from the leaching solution, precipitated and recovered before final disposal of effluents. Arsenic recovery from concentrate by leaching has not been reported in recent years, with the exception of the copper arsenate circuit at Equity Silver mine, which is no longer in operation. Production of arsenic trioxide and arsenic metal from copper smelter dusts at Sumitomo Metal Mining Company in Japan have well performed for many years. However, these operations are not preferable from economical standpoint because the complex composition of the dusts. Also, in the past years, the market for arsenic compounds like arsenic trioxide and arsenic metal have not grown, thus creating a surplus of arsenic production, however these operations are essential to the copper smelting.

On the other hand, when arsenic is not recovered, it is removed from the arsenic-bearing residues and stabilized in the form of a solid compound prior to disposal. Arsenic chemistry is complex, involving a variety of oxidation states, anionic and cationic species. Arsenic occurs as both inorganic and organic compounds and there are all commonly found in arsenic wastes, often at the same time. Oxidizing agents such as oxygen, Fe (III), $NaClO_3$, MnO_2, $K_2Cr_2O_7$, H_2O_2 or HNO_3 can be used in hydrometallurgical processes for oxidation of arsenic (III) to arsenic (V).

Arsenic is precipitated by adding lime to the solution, which is relatively cheap, obtaining a calcium arsenite/arsenate compound. However, the stability of this compound has been questioned because under the influence of atmospheric CO_2, calcium arsenate decomposes to calcium carbonate and liberates arsenic oxide in solution. Calcination of the hydroxy arsenate to produce a stable product, $Ca_3(AsO_4)_2$, are currently operating in Chilean copper smelters as mentioned in section 4.4.1.

For a long-term stability, the formation of more stable forms has been studied (i.e., arsenates of Cu, Zn, Co, Ba, Hg, etc.), but at present the industry has adopted the ferric arsenate method known as scorodite ($FeAsO_4 \cdot 2H_2O$). It was found that the molar Fe:As ratio has an effect on the solubility of precipitated arsenic-containing ferric hydroxides and that the presence of CO_2 does not increase its solubility. A minimum molar Fe:As ratio of 4 is required in the solution to favor the formation of an amorphous ferric arsenate of lower solubility (< 1 mg/L in the pH range 3–7) at ambient temperature. This process is effective for low arsenic-containing effluent. However for the fixation of arsenic in arsenic-rich solution, the application of this method would lead to the generation of a large volume of amorphous arsenic-bearing ferrihydroxide/gypsum sludge.

However, crystalline ferric arsenate (Fe/As molar ratio $\approx$ 1) is less soluble (typically < 1 ppm As at pH = 5.0) than amorphous ferric arsenate and high temperatures favor its precipitation.

Two alternatives have been proposed:

- At 150-225°C for sulfate solutions at pH<1, > 90% of arsenic precipitates using a Fe/As molar ratio between 1:1 to 9:1. However, the formation conditions in all these cases require the use of autoclaves, which are considered to be a capital-intensive technology.

- Atmospheric pressure at 95°C for sulfate solutions induced by the addition of scorodite seed, and a controlled addition of Fe^{3+}. Thus, $\approx$ 90% of arsenic precipitates from solutions containing between 5 to 10 g/L As(V).

The two sulfides As_2S_3 and As_4S_4 (corresponding to the minerals orpiment and realgar, respectively) have low solubility in acidic solutions. However, their use is not favored because of the possibility of atmospheric and bacterial oxidation liberating arsenic.

There are other metal arsenates, e.g., of Ba^{2+}, Cu^{2+} and Pb^{2+}, which are less soluble and more stable in the neutral pH region than the calcium or ferric arsenates, but these have not been seriously considered as disposal forms. Calcium phosphate arsenate with apatite structure presents low solubility and appropriate stability for disposal over the range of pH 9-12.6. Mimetite, $Pb_5(AsO_4)_3Cl$, was found to be one of the most insoluble arsenic compounds. Also, a number of other arsenic removal techniques, e.g., ion exchange, solvent extraction, membrane separations, have been investigated and/or actually are in use.

As it was shown above, several investigations have been carried out to develop a process for disposal to arsenic. However, the complex composition of these makes it difficult to attain economical feasibility, and very few processes have been applied on a large scale. In practice, arsenic has been removed from refractory gold concentrates, cobalt concentrates or copper smelter dusts by leaching and then precipitated as arsenic sulfide or ferric arsenate prior to disposal:

- High-pressure aqueous oxidation conduced in autoclaves in acid medium at 190°C and 1,600-2,100 kPa proved to be an effective method for liberating gold from its refractory ores. Arsenic forms ferric arsenate and the effluent contains < 0.3 mg/L of arsenic. This process is used at Placer Dome Canada's Campbell Gold Mine; Homestake's MacLaughlin plant, California; São Bento Mineraçao, Brazil; the Olimpias Mine in Northern Greece; and the Porgera Complex, Papua, New Guinea.

- Hydrometallurgical processes in several copper smelters treat the dust generated in the process by leaching of the dust with H_2SO_4 at 25-130°C to recover Cu, Zn or Pb from the solution, then precipitation of arsenic as ferric arsenate or arsenic sulfide for disposal. Air, H_2O_2, or $KMnO_4$ are used for oxidation of As (III) to As (V) at room temperature. At

Kennecott Copper Company in USA, arsenic is reduced to $HAsO_2$ using $NaHSO_3$ then precipitated with NaHS or $FeSO_4$.

- Acid or alkaline leaching in presence of an oxidizing agent has been used to treat cobalt ores or concentrates:
  - ☐ Acid leaching at 200°C and 1200 kPa oxygen pressure, known as the Calera process has been applied for the recovery of cobalt from a sulfarsenide ore. While arsenic is precipitated as ferric arsenate.
  - ☐ Oxidation in presence of NaOH results in solubilizing both arsenic and sulfur, while the metal values remain undissolved. Treatment is carried out at 115°C and 840 kPa oxygen pressure. Arsenic can be removed from the leach solution by precipitation with lime to give calcium arsenate, or with H_2S to give arsenic sulfide.

The Chilean mining industry is associated with several environmental problems: air pollution due to SO_2, particulate matter, and arsenic emissions, water pollution due to liquid effluents containing particulate matter, dissolved metals and acids, soil contamination and risk posed by abandoned mining sites and tailing dams. The copper smelters are the main source of SO_2, arsenic and particulate matter emissions. There have been reductions in these amounts released into the atmosphere in recent years, but the problem remains serious. The Government of Chile has promulgated the following laws:

- Decree Law 185 to regulate the smelter operations that emit to the atmosphere quantities higher or equal to 3 t/d of sulfur dioxide, or 1 t/d of particulate matter. It makes it mandatory to present decontamination plans, determined demands on information reporting and, in some smelters, it forces management to report plans for controlling high SO_2 concentration episodes.

- Decree Law 165 regulates arsenic emitted to the atmosphere from copper smelters.

- A decontamination plan has been implemented on smelters for reducing emissions of SO_2, particulate matter and arsenic. The project under development will incorporate gas handling systems and sulfuric acid plants. For example in Codelco's smelters:

    - ☐ Four sulfuric acid plants began to operate in Chuquicamata smelter from 1985 to 1998, with a total capacity around 5,600 t/d, which have allowed capturing around 87% of the sulfur and 90% of the arsenic.

    - ☐ At Caletones smelter, a sulfuric acid plant with a capacity of 1,500 t/d has been operating since August 1998, having the capability to capture 37% of the sulfur and 50% of the arsenic.

    - ☐ A new acid plant for Potrerillos smelter with a 1,500 t/d capacity began operation at the end of 1999.

    - ☐ All the smelters have effluents treatment plants for the arsenic disposal either as ferric arsenate or calcium arsenate/arsenite.

    - ☐ El Teniente and Chuquicamata smelters have arsenic-containing dusts treatment plants, where arsenic is disposed of in the form of ferric arsenate.

    - ☐ There is arsenic trioxide production as a by-product of the copper concentrate produced at the El Indio mine.

RECOMMENDATIONS FOR FURTHER WORK:

Arsenic should be incorporated as an important parameter in the mine design for ore extraction. The production of concentrates with variable arsenic concentrations requires the design and development of new processes for the treatment of the concentrates with high arsenic concentrations. Therefore, the study of the following variables should be analyzed:

- New technology available: the size, capital cost and operating life of the arsenic treatment plant.

- The relative cost of reagents such as lime or ferric sulfate as well as other operating cost.

- The cost for disposal of residues from the process. In some instances a portion of the residues produced may be sold or recycled to the smelting process.

- Such an economic study was impossible to carry out in this thesis because of the secrecy that characterizes the metallurgical industry around the world regarding costs. Although many contacts and demands were made by the author, very few cost figures were provided from the metallurgical industry.

It is interesting to note that there has not been significant and innovative improvements in the methods for removing arsenic from process and effluents solutions in the last years. However, it will be interesting to test on industrial effluents the scorodite precipitation technique developed by the Hydrometallurgy Group of McGill University, possibly on a continuous pilot plant scale. This method does not require an autoclave, therefore, the capital investment can be appreciably reduced.

Also, another important problem facing copper smelters today is the generation of SO_2 emissions containing variable concentrations of arsenic trioxide. Although most smelters have been successful in preventing environmental pollution by developing various pollution control technologies, yet the problem remains serious. It is, therefore, necessary to further reduce the quantity of SO_2 discharged and new uses of sulfur must be developed because demand for sulfuric acid and sulfur in the world is sluggish.

Chile could be in the near future the world's largest producer of arsenic, due to environmental regulations that limit the arsenic emitted from smelters. Therefore, a good knowledge of arsenic trioxide and arsenic metal production economics should be a guide for investing in the construction of arsenic treatment plants, and new utilisations for arsenic must be developed.

REFERENCES

Accardo, S., Sweeney, M., and Chatwin, T., 1995, "Treatment of Sutter Gold Venture's Mine Water to Remove Arsenic with Activated Alumina", in *New Remediation Technology in the Changing Environmental Arena,* Society for Mining, Metallurgy and Explotation, Littleton, CO, pp. 105-110.

Achurra, G., Jefe Ingeniería y Planificación Fundición Caletones, Codelco-Chile, private communication dated 1999/11/15.

Adams, R., and Sinha, U., 1990, "Improving the Quality of Continuous Copper Rod", *JOM,* 42:5, pp. 31-34.

AllChem Industries, 2000, "Current Price Indications", dated 2000/01/7.
Page Web: www.allchem.com/price.html

Alvarado, R., and Godoy, J., 1999, "New Strategic Scope of the Caletones Smelter Development", *Copper 99-Cobre 99 International Conference,* Volume V: Smelting Operations and Advances, D.B. George, W.J. Chen, P.J. Mackey, and A.J. Weddick (Editors), The Minerals, Metals & Materials Society, Phoenix, AZ, pp. 47-55.

ANADIGICS, 1998, "*Anadigics Inc. Annual Report*". Page web: http://www.anadigics.com

Anderson, M.A., Ferguson, J.F., and Gavis, J., 1976, "Arsenate Adsorption on Amorphous Aluminium Hydroxide", *J. Colloid & Interface Sci.,* 54:3, pp. 391-399.

Anderson, D.G., Cornfield, J.A., and Williams, G.R., 1991, "Waterbased Fixed Preservatives", in *The Chemistry of Wood Preservation,* R. Thompson (Editor), The Royal Society of Chemistry, UK, pp. 101-116.

Araya, R., Codelco-Chile, Division El Teniente, private communication dated 1999/06/30.

AWPI, 1999, "Construction Guidelines for Timber Piling Projects", *AWPI Pole, Piling and Timber Council.* Page web: http://www.awpi.org/ppt/home.html

Baboudjian, V., Desroches, C., and Godbehere, P., 1995, "Treatment of Complex Feeds at Noranda Copper Smelting and Refining, in *Proceedings-27th Annual Meeting of the Canadian Mineral Processors,* CIM, Ottawa, Canada, pp. 363-378.

Baradel, A., Guerriero, R., Meregalli, L., and Vittadini, I., 1986, "Extraction of As from Copper Refining Electrolyte", *JOM*, 38:2, pp. 32-37.

Bencko, V., 1987, "Arsenic", in *Genotoxic and Carcinogenic Metals: Environmental and Occupational Occurrence and Exposure.* Advances in Modern Environmental Toxicology, Volume XI, Fischbein, Furst and Mehlman (Editors), Princeton Scientific Publishing Co., Princeton, NJ.

Berezowsky, R.M.G.S., Haines, A.K., and Weir, D.R., 1988, "The Sao Bento Gold Project", in *Projects '88*, 18th Annual Hydrometallurgical Meeting of the Canadian Institute of Mining and Metallurgy, Edmonton, Alberta.

Berezowsky, R.M.G.S., Collins, M.J., Kerfoot, D.G.E., and Torres, N., 1991, "The Commercial Status of Pressure Leaching Technology", *JOM*, 43:2, pp. 9-15.

Biswas, A.K., and Davenport, W.G., 1994, *Extractive Metallurgy of Copper*, Oxford, England.

Bolton, G.L., and Weir, D.R., 1994, "Autoclave Processing of Gold and Zinc", in *100th Annual Northwest Mining Association Convention*, Spokane, WA.

Borgono, J.M. and Greiber, R., 1971, "Epidemiological study of arsenicism in the city of Antofagasta", in *Trace Substances in Enviromental Health*, V.D.D. Hemphill (Editor), University of Missouri, Columbia, MO., p. 13.

Brewis, T., 1984, "Japanese Smelters", *Mining Magazine*, 151:4, pp. 430-459.

Brierley, C.L., 1995, "Bacterial Oxidation", *E&MJ*, 196:5, pp. 42-44.

Brown, C.C., and Chu, K.C., 1983a, "Implications of the Multistage Theory of Carcinogenesis Applied to Occupational Arsenic Exposure", *J. Natl. Cancer Inst.*, 70, pp. 455-463.

Brown, C.C., and Chu, K.C., 1983b, "A New Method for the Analysis of Cohort Studies: Implications of the Multistage Theory of Carcinogenesis Applied to Occupational Arsenic Exposure, *Environ. Health Perspect.*, 50, pp. 293-308.

Brown, E.J., Luong, H.Y., and Forschaug, J.M., 1983, "Geomicrobiology of Arsenic Associated with Gold Deposits in Alaska", in *Recent Progress in Biohydrometallurgy*, G. Rossi and A.E. Torma (Editors), Associazione Mineraria Sarda, Italy, pp. 571-580.

Brown, F.W., Hunt, P.R., and Halbe, D.N., 1990, "Fluosolids Roasting of Arsenopyrite Ore – Lancefield Wastern Australia", in *Proceedings of the Gold'90 Symposium*, D.M. Hausen, D.N. Halbe, E.U. Petersen, and W.J. Tafuri (Editors), Salt Lake City, UT, pp. 419-433.

Buckingham, L., Wilson, L., Thomas, K., and Frostiak, J., 1999, "Operation and Improvements at the El Indio Roasting Facility", *Proceeding-31st Annual Meeting of the Canadian Mineral Processors*, CIM, Ottawa, Canada, paper 1.

Campos, R., Miranda, S., and Smith, T.J.A., 1998, "Refimet Smelter Operation and Development", in *Sulfide Smelting '98,* J.A. Asteljoki and R.L. Stephens (Editors), TMS Annual Meeting, San Antonio, TX, pp. 519-534.

Castro, S.H., and Muñoz, P., 2000, "Removal of Arsenic (III) in Solution by Co-precipitation of Calcium Arsenite and Calcium Hydroxide", in *V International Conference on Clean Technology for the Mining Industry,* Vol. I: Waste Treatment and Environmental Impact in the Mining Industry, M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile.

CBC News, 1999a, "Report Recommends Arsenic Warnings in Yellowknife".
Page web: http://cbc.ca/cgi-bin/templates/view.cgi?/news/1999/07/13/arsenic990713

CBC News, 1999b, "Miramar Finally Purchases Giant Mine".
Page web: http://cbc.ca/cgi-bin/templates/view.cgi?/news/1999/12/15/ns_vk1

CBC News, 1999c, "Gold Mine Clean-up to Cost $16 Million".
Page web: http://cbc.ca/cgi-bin/templates/view.cgi?/news/1999/12/08/giant991208

Chenier, J., Morin, G., and Verhelst, D., 1992, "Minor Element Behaviour in the Kidd Creek Copper Smelter", in *Proceedings of the International Symposium on Non-Ferrous Pyrometallurgy: Traces Metals, Furnace Practices and Energy Efficiency*, R. Bergman (Editor), CIM, Edmonton, Canada, pp. 27-44.

Clarke, N., and Wilson, D.J., 1983, *Foam Flotation: Theory and Application,* Marcel Dekker (Editor), New York, NY.

Coakley, G.J., 1997, "The Mineral Industry of Ghana - 1996", U.S. Geological Survey.
Page web: http://minerals.usgs.gov/minerals/pubs/country/9213096.pdf

Coakley, G.J., "Arsenic in Namibia", U.S. Geological Survey, private communication dated 1999/05/25.

COCHILCO, 1996, "El Mercado Nacional de Concentrados de Cobre", *Vision Minera,* Comisión Chilena del Cobre, Año III, N° 4.

COCHILCO, 1998, "Cronogramas de Reducción de Emisiones Asociados a los Planes de Descontaminación", Comisión Chilena del Cobre.
Page web: http://www.cochilco.cl/ambiente/cronogr.html

COCHILCO, 1999, "Producción Mundial de Cobre de Mina", Comisión Chilena del Cobre. Page web: http://www.cochilco.cl/estadist/tabla7.htm

Cocquerel, M. A. and Shaw, M. F., 1983, "Arsenic Control in Modern Smelting Processes", in *Sulfur Dioxide: Control in Pyrometallurgy*, pp. 961-975.

CODELCO, 1998, "Medio Ambiente y Comunidades", Memoria Anual 1998,Codelco-Chile. Page web: http://codelcochile.com/corporacion/memorias/memo98.pdf

Comba, P., Dahnke, D.R., and Twidwell, L.G., 1988, "Removal of Arsenic from Process and Wastewater Solutions", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 305-319.

CONAMA, 1998, "Planes de Descontaminación Fundiciones de Cobre de Chile".
Page web: http://www.conama.cl/Regiones/2/planes_de_desc.htm

CONAMA, 1999, "Norma de Emisión para la Regulación del Contaminante Arsénico Emitido al Aire, Ministerio Secretaría General de la Presidencia – Comisión Nacional del Medio Ambiente. Page web: www.conama.cl/documentos/planes_y_normas/arsenico.doc

CONAMA, 2000, "Aprueba Anteproyecto de Reformulación del Plan de Descontaminación para la Zona Circundante a la Fundición Chuquicamata de la División Chuquicamata de Codelco Chile", Ministerio Secretaría General de la Presidencia – Comisión Nacional del Medio Ambiente.
Page web: http://www.conama.cl/nuestra_institucion/areas_de_trabajos/u_planes_norma/antepro_chuquicamata.htm

Contreras, L., Reyes, P., Martinich, B, and Bustamante, R., 1999, "Gas Handling and Cleaning at the Potrerillos Smelter", in *Copper 99-Cobre 99 International Conference*, Volume V: Smelting Operations and Advances, D.B. George, W.J. Chen, P.J. Mackey, and A.J. Weddick, (Editors), TMS, Phoenix, AZ, pp. 119-132.

Da Silva, E.J., Haines, A.K., Carvalho, T.M., de Melo, M.P., and Doyle, B.N., 1989, "Process Selection, Design, Commissioning and Operation of the Sao Bento Mineracao Refractory Gold Ore Treatment Complex", in *Gold Forum on Technology and Practices – World Gold'89,* Reno, NV.

Dainichi, 1998, "Arsenic in Drinking Water-Treatment Technologies: Removal".
Page web: http://www.dainichi-consul.co.jp/english/arsenic/treat1.htm

Dalewski, F., 1999, "Removing Arsenic from Copper Smelter Gases", *JOM*, 51:9, pp. 24-26.

Dambies, L., Roze, A., Roussy, J., and Guibal, E., 1999, "As(V) Removal from Dilute Using MICB (Molybdate-impregnated chitosan beads)", in *Biohydrometallurgy and the Environment Toward the Mining of the* 21^{st} *Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part B: Molecular Biology, Biosorption, Bioremediation, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, pp. 277-287.

Danielsson, L., 1965, "Adsorption of a Number of Elements from Sulfuric Acid Solution by Anion Exchange", *Acta Chem. Scand.*, 19:3, pp. 670-678.

De Schepper, A., 1985, "MHO Solvent Extraction Process for Removal of Arsenic from Olen Copper Tankhouse Bleed", in *Extraction Metallurgy '85,* A.G. Moncrieff (Editor), IMM, London, England, pp. 167-188.

Demopoulos, G.P., Droppert, D.J., and Van Weert, G., 1994, "Options for the Immobilization of Arsenic as Crystalline Scorodite", in *Impurity Control and Disposal in Hydrometallurgical Process,* B. Harris and E. Krause (Editors), CIM, Montreal, Canada, pp. 57-69.

Dewalens, J., Heerman, L., and Van Simaeys, L., 1975, "The Codeposition of Copper and Arsenic from H_2SO_4-$CuSO_4$-As_2O_3 Solutions. Electrochemical Formations of Copper Arsenates", *J. Electrochem. Soc.*, 122:4, pp. 477-482.

Díaz, B., Sánchez, G., and Moreno, A., 1997, "Teniente Converter Technology Applied Las Ventanas Smelter", in *Teniente Converter Technology Workshop: Commemoration of its 20th Anniversary,* organised by Codelco-Chile, Division El Teniente, V region, Chile.

Donnelly, J.R., and Evans, C.M., 2000, "Copper Smelter Acid Plant Effluent Treatment Concepts", in *V International Conference on Clean Technology for the Mining Industry,* Vol. I: Waste Treatment and Environmental Impact in the Mining Industry, M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile.

Drever, J., 1997, "Heavy Metals and Metalloids", in *The Geochemistry of Natural Waters: Surface and Groundwater Environments,* pp. 175-196.

Droppert, D.J., 1996, "The ambient Pressure Precipitation of Crystalline Scorodite ($FeAsO_4{\cdot}2H_2O$) From Sulphate Solutions", *Master of Engineering Thesis*, Dep. of Mining and Metallurgical Engineering, McGill University, Montreal, Canada.

Duran, M.A., 1999, "Planes Desarrollo Chagres", in *Curso: Pirometalurgia del Cobre,* Instituto de Ingenieros de Minas de Chile, Antofagasta, Chile.

Dutrizac, J.E., Jambor, J.L., and Chen, T.T., 1987, "The Behaviour of Arsenic during Jarosite Precipitation: Reaction at 150°C and the Mechanism of Arsenic Precipitation", *Canadian Metall. Quart.*, 26:2, pp. 103-115.

Edelstein, D.L., 1994, "Arsenic", in *Minerals Yearbook*, Volume I, Metals and Minerals, U.S. Department of the Interior, U.S. Bureau of Mines, pp. 77-80.
Page web: http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/160494.pdf

Edelstein, D.L., 1995, "Arsenic", in *Minerals Yearbook*, Volume I, Metals and Minerals, U.S. Department of the Interior, U.S. Geological Survey, pp. 71-74.
Page web: http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/160495.pdf

Edelstein, D.L., 1996, “Arsenic”, in *Minerals Yearbook*, US Geological Survey.
Page web: http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/160496.pdf

Edelstein, D.L., 1998, “Copper”, in *Minerals Yearbook*, US Geological Survey.
Page web: http://minerals.usgs.gov/minerals/pubs/commodity/copper/240498.pdf

Edelstein, D.L., 2000, “Copper”, in *Mineral Commodity Summaries*, US Geological Survey. Page web: http://minerals.usgs.gov/minerals/pubs/commodity/copper/240300.pdf

Edwards, C.R., 1985, “The Equity Silver Leach Plant”, *CIM Bulletin,* 78:884, pp. 84-93.

Edwards, C.R., 1991, “The Recovery of Metal Values from Process Residues”, *JOM*, 43:6, pp. 32-33.

Egawa, H., Nonaka, T., and Maeda, H., 1985, “Removal and Recovery of Arsenic Ion in Geothermal Power Waste Solution with Chelating Resines”, *Sep. Sci. Technol.*, 20:9-10, pp. 653-664.

Eguez, H.E., and Cho, E.H., 1987, “Adsorption of Arsenic on Activated Charcoal”, *JOM,* 39:7, pp. 38-41.

Enterline, P.E., and Marsh, G.M., 1980, “Mortality Studies of Smelter Workers”, *Am. J. Ind. Med.*, 1, pp. 251-259.

Enterline, P.E., and Marsh, G.M., 1982, “Cancer Among Workers Exposed to Arsenic and Other Substances in a Copper Smelter”, *Am. J. Epidemiol.*, 116, pp. 895-911.

Environment Agency of Japan, 1999, “Laws and Regulations : Environmental and Emissions Standards”, Government of Japan. Page web: http://www.eic.or.jp/eanet/en/index.html

Environment Canada, 1977, “Metal Mining Liquid Effluent Regulations and Guidelines”, Environmental Protection Service, Report N° EPS 1-WP-77-1.

Environment Canada, 1992, “ARET: Accelerated Reduction/Elimination of Toxics”.
Page web: http://www.ec.gc.ca/aret/homee.html

Environment Canada, 1996, “Environmental Management in Chile-Report”, Chapter 4.
Page web: http://www.naaec.gc.ca/english/canchile/report/chilerepch4a_e.htm

Environment Canada, 1999, “Environmental Leaders 3: ARET”, Voluntary Action on Toxic Substances, A Progress Report.
Page web: http://www.ec.gc.ca/aret/reports/aret_el3_e.pdf

Fabian, H., Richarson, H.W., Habashi, F., and Besold, R., 1997, “Copper”, in *Handbook of Extractive Metallurgy,* Vol. II, F. Habashi (Editor), VHC- Wiley, pp. 491-579.

Fan, Y., Padilla, R., Sanchez, M., and Wilkomirsky, I., 1996, "Arsenic Removal from Copper Concentrate by Neutral and Oxidizing Roasting", in *Clean Technology for the Mining Industry*. M. A. Sanchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 299-311.

Farias, L., Reghezza, A., and Cruz, A., 1993, "Tratamiento Hidrometallurgico de Polvos de Fundicion en la División Chuquicamata de Codelco-Chile: Situación Actual y Perspectivas", in *III Jornadas de Metalurgia del Norte Grande*, Antofagasta, Chile.

Farias, L., Reguezza, A., Cruz, A., Matta, J., and Guzmán, A., 1996, "Arsenic Confinement in Chuquicamata Hydrometallurgical Processes", in *III International Conference on Clean Technology for the Mining Industry*. M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 315-321.

Ferreira, P.M., Knott-Craig, K., and Boydell, D.W., 1989, "Roasting of Refractory Au Concentrates at New Consort", *E&MJ*, 190:12, pp. 26-30.

Filippou, D., and Demopoulos, G.P., 1997, "Arsenic Immobilization by Controlled Scorodite Precipitation", *JOM*, 49:12, pp. 52-55.

Frost, R.R., and Griffin, R.A., 1977, "Effect of pH on Adsorption of Arsenic and Selenium from Landfill Leachate by Clay Minerals", *Soil Sci. Soc. Am. J.*, 41, pp. 53-57.

Frostiak, J., Raudsepp, R., and Stauffer, R., 1990, "The Application of Pressure Oxidation of the Campbell Red Lake Mine", in *Randol Forum*, Squaw Valley, CA.

Frostiak, J., and Haugrud, B., 1995, "Start up and Operation of the Campbell Red Lake Gold Pressure Oxidation Plant", private communication with Roman M. Berezowsky dated 1999/09/29.

GaAsNet, 1999, "Semiconducting GaAS", *The GaAs Electronics Industry Resources*.
Page web: http://www.gaasnet.com/categories/SCGAAS.html

Gabb, P.J., Howe, D.L., Purdie, D.J., and Woerner, H.J., 1995, "The Kennecott Smelter Hydrometallurgical Impurities Process", in *Copper 95-Cobre 95 International Conference*, Volume III: Electrorefining and Hydrometallurgy of Copper, W.C. Cooper, D.B. Dreisinger, J.E. Dutrizac, H. Hein and G. Ugarte (Editors), Metallurgical Society of CIM, Santiago, Chile, pp. 591-606.

Gabb, P.J., and Davies, A.L., 1999, "The Industrial Separation of Copper and Arsenic as Sulfides", *JOM*, 51:9, pp. 18-19.

Gagan, E.W., 1979, "Arsenic Emissions and Control Technology: Gold Roasting Operations", *Economical and Technical Review*, Report EPS 3-AP-79-5, Air Pollution Control Directorate, Environment Canada, Ottawa.

Gavrichev, V.S., et al., 1969, "Extraction of Arsenic from Hydrochloric Acid Solutions by some Oxygen Containing Solvents", *Izv. Vyssh. Ucheb. Zaved. Khim. Tekhnol.,* 12:8, pp. 1023-1026.

Godbehere, P., Pinard, D., and Guimont, J., 1995, "Development of a Treatment Process for an Arsenic-bearing Weak Acid Effluent Using Iron and Zinc Derived from Acid Mine Drainage and Smelter Precipitator Dust", in *Copper 95-Cobre 95 International Conference*, Volume II: Mineral Processing and Environment, A. Casali, G.S. Dobby, M. Molina and W.J. Thoburn (Editors), Metallurgical Society of CIM, Santiago, Chile, pp. 377-389.

González, F., Ponce, R., Díaz, B., and Sanhueza, J., 1995, "Environment and Industrial Reconversion at Las Ventanas Smelter and Refinery", in *Copper 95-Cobre 95 International Conference*, Volume II: Mineral Processing and Environment, A. Casali, G.S. Dobby, M. Molina and W.J. Thoburn (Editors), Metallurgical Society of CIM, Santiago, Chile, pp. 361-367.

González, V.L.E., and Monhemius, A.J., 1988, "Mineralogy of Arsenates Relating to Arsenic Impurity Control", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS, Phoenix, AZ, pp. 405-453.

Grossman, H., Hanusch, K., Herbst, K.A., Rose, G. and Wolf, H.U., 1997, "Arsenic", in *Handbook of Extractive metallurgy*, Vol. II, F. Habashi (Editor), VHC- Wiley, pp. 795-822

Gupta, S.K., and Chen, K.Y., 1978, "Arsenic Removal by Adsorption", *J. Water Pollution Control Federation,* 50, pp. 493-506.

Gurmendi, A.C., 1998, "The Mineral Industry of Peru - 1997", U.S. Geological Survey. Page web: http://minerals.usgs.gov/minerals/pubs/country/9519097.pdf

Habashi, F., 1986, "Oxidation of Sulfides", in *Principles of Extractive Metallurgy,* Volume 3: Pyrometallurgy, Gordon and Breach Science Publishers, New York. pp. 171-188.

Habashi, F., 1999, "Arsenides", in *Textbook of Hydrometallurgy,* 2nd Edition, pp. 335-340, Laval University, Quebec City, Canada.

Haibei, W., 2000, Beijing General Research Institute of Mining and Metallurgy, private communication to F. Habashi dated 2000/06/14.

Harris, G.B. and Monette, S., 1985, "A Hydrometallurgical Approach to Treating Copper Smelter Precipitator Dusts", in *Complex Sulfides: Processing of Ores, Concentrates and By-Products,* A.D. Zunkel, R.S. Boorman, A.E. Morris and R.J. Wesely (Editors), Metallurgical Society of AIME, Warrendale, PA, pp. 361-375.

Harris, G.B., and Monette, S., 1988, "The Stability of Arsenic-Bearing Residues", in *Arsenic Metallurgy Fundamentals and Applications,* Reddy, R.G., Hendrix, J.L., and Queneau, P.B., eds., TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 469-488.

Harris, G.B., 2000, "The Removal and Stabilization of Arsenic from Aqueous Process Solutions: Past, present, and Future", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 3-20.

Health Canada, 1992, "Arsenic", in *Guidelines for Canadian Drinking Water Quality".* Page web: http://www.hc-sc.gc.ca/ehp/ehd/catalogue/bch_pubs/dwgsup_doc/arsenic.pdf

Higgins, I., Welch, K., Oh, M., Bond, G., and Hurwitz, P., 1981, "Influence of Arsenic Exposure and Smoking on Lung Cancer Among Smelter Workers: A Pilot Study", *Am. J. Ind. Med.*, 2, pp. 33-41

Hino, J., 1995, "Environmental Pollution Control Technology in Copper Smelting", *Metallurgical Review of MMIJ,* 12:2, pp. 1-14.

Hino, J., Kawabata, T., Miyamoto, K., and Yamaki, T., 1995, "Removal and Recovery of Minor Elements in Copper Smelting", in *Copper 95-Cobre 95 International Conference,* Volume III: Electrorefining and Hydrometallurgy of Copper, W.C. Cooper, D.B. Dreisinger, J.E. Dutrizac, H. Hein and G. Ugarte (Editors), Metallurgical Society of CIM, Santiago, Chile, pp. 617-627.

Hoffmann, J., 1993, "Remediating Copper Smelter Dusts: The Arsenic Problem", *JOM,* 45:4, pp. 30-31.

Household, 1997: "The Use of Arsenic in Pest Control".
Page web: http://www.nccnsw.org.au/member/tec/projects/tcye/detail/Household/Arsen_pest_30.html

Huang, C.P., and fu, P.L.K., 1984, "Treatment of As (V) Containing Water by the Activated Carbon Process", *J. Water Poll. Control Fed.*, 56:3, pp. 233-242.

Hussain, I., 1999, "Arsenic Contamination of Ground Water in Bangladesh: A Briefing Paper", *Ministry of Health and Family Welfare Bangladesh.*
Page web: http://phys4.harvard.edu/~wilson/arsenic_project_ground_water.html

IARC, 1980, "Arsenic and Arsenic Compounds", in *IARC Monographs,* Chapter 5. Summary of Data Reported and Evaluation, Vol. 23, p. 39-141.
Page web: http://193.51.164.11/htdocs/monographs/vol23/arsenic.html

Ibach, R.E., 1999, "Wood Preservation", in *Wood Handbook: Wood as an Engineering Material,* Forest Products Society, USA, Chapter 14.

Jeffrey, J.D., 1996, "El Indio and Tambo", *Mining Magazine,* 153:5, pp. 268-276.

Jian, L., 1998, "Study of Extracting Arsenic From Electrolyte Solution Using Supported Liquid Membrane", in *ICHM'98: Proceedings of the Third International Conference on Hydrometallurgy",* Y. Xianwan, C. Qiyuan and H. Aiping (Editors), The Nonferrous Metals Society of China, Kunming, China, pp. 489-491.

Jiaoyong, Y., Daxing, L., Huifang, Z., and Kaixi, J., 1990, "Improvement of Removing Arsenic from Copper Electrolyte with Solvent Extraction", in *Solvent Extraction 1990,* Proceedings of the International Solvent Extraction Conference (ISEC'90), Part B, Process Metallurgy 7B, T. Sekine (Editor), pp. 1205-1210.

Kaixi, J., Lan, L., Daxing, L., and Haibei, W., 1998, "Hydrometallurgical Processes for Arsenous Sulfide Residues", in *ICHM'98: Proceedings of the Third International Conference on Hydrometallurgy",* Y. Xianwan, C. Qiyuan and H. Aiping (Editors), The Nonferrous Metals Society of China, Kunming, China, pp. 603-608.

Kartanjian, H., and Koller, Ch. A., 1996, "Use of Arsenic Trioxide in the Treatment of APL", Remission Induction in Relapsed Patients and Pharmacokinetics.
Page web: http://www.mdacc.tmc.edu/~leukemia/flash/arsenic.html

Kholmanskikh, Y.B., 1971, "Ion Exchange Extraction of Antimony (III) and Arsenic (V) from Strongly Acid Solutions", *Tr. Ural. Nauch. – Issled. Proekt. Inst. Medn. Prom.,* 14, pp. 215-219.

Kontopoulos, A., and Stefanakis, M, 1989, "Process Selection for the Olympias Refractory Gold Concentrate", in *Precious Metals*, M.C. Jha, and S.D. Hill (Editors), TMS, Warrendale, PA, pp. 179-209.

Kontopoulos, A., and Stefanakis, M, 1990, "Process Options for Refractory Sulphide Gold Ores: Technical Environmental and Economic Aspects", in *EPD Congress 90,* Gaskell, D.R. (Editor), TMS, Warrendale, PA, pp. 393-412.

Kontopoulos, A., and Adam, K., 1992, "Arsenic in Extractive Metallurgy: Environmental Problems and Solutions", *Transactions of the Technical University of Košice*, Volume 2, Special Issue, pp. 144-152.

Kozmin, Y.A., et al., 1970, "Experimental-Industrial Testing of an Alkaline Electrolysis Process for Treating Lead Dusts", *Tsvet. Met.,* 43:9, pp. 45-48.

Kramer, D.A., 1998, "Gallium", in *Minerals Yearbook,* U.S. Geological Survey.
Page web: http://minerals.usgs.gov/minerals/pubs/commodity/gallium/460498.pdf

Krause, E., and Ettel, V.A., 1985, "Ferric Arsenate Compounds: Are They Environmentally Safe? Solubilities of Basic Ferric Arsenates", in *Impurity: Control and Disposal,* 15th Annual Hydrometallurgical Meeting, Vancouver, Canada, paper 5.

Krause, E., and Ettel, V.A., 1987, "Solubilities and Stabilities of Ferric Arsenates", in *Crystallization and Precipitation,* Proceedings of the International Symposium, G.L. Strathdee, M.O. Klein and L.A. Melis (Editors), Saskatoom, Canada, pp. 195-210.

Krause, E., and Ettel, V.A., 1989, "Solubilities and Stabilities of Ferric Arsenate Compounds", *Hydrometallurgy,* 22, pp. 311-337.

Kunter, R.S., and Bedal, W.E., 1992, "Chloride Process Treatment of Smelter Flue Dusts", *JOM,* 44:12, pp. 35-38.

Kunter, R.S., 1993, "The Cashman and Other Hydrometallurgical Process Treatments of Polymetallic Arsenical Dusts, Sludges, and Wastes", in *Mercury and Arsenic Wastes: Removal, Recovery, Treatment, and Disposal,* Pollution Technology Review N° 214, US EPA (Editor), NJ, pp. 92-97.

La Tercera, 1999, "Arsénico recorre cuerpos de habitantes de Chiu Chiu", Crónica Nacional. Page Web: http://www.tercera.cl/diario/1999/07/12/12.15.3a.CRO.ARSENICO.html

Laguitton, D., 1976, "Arsenic Removal from Gold-mine Waste Waters: Basic Chemistry of the Lime Addition Method", *CIM Bulletin,* 69:773, pp. 105-109.

Landsberg, A., Mauser, J.E., and Henry, J.L., 1980, "Behavior of Arsenic in a Static Bed During Roasting of Copper Smelter Feed", in *Report of Investigations 8493*, United States Department of the Interior, Bureau of Mines, Washington, DC.

Lange, C., 1999, "Tratamiento de Efluentes Líquidos", in *Segunda Mesa Redonda Plantas de Acido Sulfúrico,* Escuela Ingeniería Química (Editor), Universidad Católica de Valparaíso, La Serena, Chile.

Leach, R.M., 1999, "An Alternative to Arsenic Disposal: Wood Preservation", *JOM*, 51:9, p. 34.

Leckie, J.O., Merrill, D.T., and Chow, W., 1985, "Trace Element Removal from Power Plant Waste Streams by Adsorption/Coprecipitation with Amorphous Iron Hydroxide", in *A. I. Ch. E. Symposium Series,* 81:243, pp. 28-42.

Lee-Feldstein, A., 1983, "Arsenic and Respiratory Cancer in Humans: Follow-up of Copper Smelter Employees in Montana, *J. Natl. Cancer Inst., 70,* pp. 601-609

Lee-Feldstein, A., 1986, "Cumulative Exposure to Arsenic and its Relationship to Respiratory Cancer Among Copper Smelter Employees", *J. Occup. Med., 28,* pp.296-302.

Lefebvre, M.S.M., and Robins, R.G., 1985, "Membrane Separations of Arsenic from Hydrometallurgical Process Streams", in *Impurity: Control and Disposal,* 15th Annual Hydrometallurgical Meeting, Vancouver, Canada, paper 10.

Lepkowski, W., 1998, "Arsenic Crisis in Bangladesh", *C&EN Washington,* November 16, pp. 27-29.

Levine, R.M., 1996a, "The Mineral Industry of Georgia", U.S. Geological Survey. Page web: http://minerals.usgs.gov/minerals/pubs/country/9415096.pdf

Levine, R.M., 1996b, "The Mineral Industry of Kazakstan", U.S. Geological Survey. Page web: http://minerals.usgs.gov/minerals/pubs/country/9422096.pdf
Liao, H.P., "Process for Removing Arsenic from Aqueous Mediums", *US Patent 4,201,667,* May 1980.

Lindkvist, G., and Holmström, Å., 1983, " Roasting of Complex Concentrates with High Arsenic Content", in *Advanced in Sulfide Smelting,* Vol. 2, H.Y. Sohn, D.B. George and A.D. Zunkel (Editors), AIME Meeting, pp. 451-472.

Loebenstein, J.R., 1992, "Arsenic", in *Minerals Yearbook,* Vol. I, Metals and Minerals in 1991, US Department of the Interior, Bureau of Mines, pp. 77-80.

Loebenstein, J.R., 1994, "The Materials Flow of Arsenic in the United States", Bureau of Mines, *Information Circular 9382.*
Page web: http://greenwood.cr.usgs.gov/pub/min-info-team/usbm-ic/ic-9382/arsenic.pdf

Lubin, J.H., Pottern, L.M., Blot, W.J., Tokudome, S., Stone, B.J., and Fraumeni, J.R., Jr, 1981, "Respiratory Cancer among Copper Smelter Workers: Recent Mortality Statistics, *J. Occup. Med.*, 23, pp. 779-784.

Lyday, T.Q., 1998, "The Mineral Industry of Philippines - 1997", *Minerals Yearbook,* U.S. Geological Survey. Page web: http://minerals.usgs.gov/minerals/pubs/country/9326097.pdf

Mackey, P.J., Vogt, J.A. and Balfour, G.C., 1979, "Current Converter Practice at the Horne Smelter", in *Copper and Nickel Converters,* R. E. Johnson (Editor), 108th AIME Annual Meeting, New Orleans, LA, pp. 357-390.

Madsen, B.W., and Martin, D.A., 1983, "Selective Recovery of Arsenic from Aqueous Solutions with Hydrated Titanium Dioxide", *Report RI8756,* US Bureau of Mines.

Maeda, S., et al., 1985, "Bioaccumulation of Arsenic by Freshwater Algae and the Application to the Removal of Inorganic Arsenic from an Aqueous Phase", Part II, *Sep. Sci. Technol.,* 20:2-3, pp. 153-161.

Malloy, P., and Tapper, R.P., 1978, "Dickenson Mines Limited", in *Milling Practice in Canada,* D.E. Pickett (Editor), CIM Special Volume 16, pp. 58-59.

Mast, E.D., Arrián, J., and Benavides, J., 1999, "Concentrate Injection and Oxygen Enrichment in Peirce Smith Converters at Noranda's Altonorte Smelter", *Copper 99-Cobre 99 International Conference,* Volume V: Smelting Operations and Advances, D.B.

George, W.J. Chen, P.J. Mackey and A.J. Weddick, (Editors), TMS, Phoenix, AZ, pp. 433-445.

Matis, K.A., Zouboulis, A.I., Malamas, F.B., Ramos, M.D., and Hudson, M.J., 1997, "Flotation Removal of As(V) Onto Goethite", *Environmental Pollution,* 97:3, pp. 239-245.

Maycock, A.R., Nahas, W., and Watson, T.C., 1990, "Review of the Design and Operation of Roasters for Refractory Gold Bearing Materials", in *Proceedings of the Gold'90 Symposium,* D.M. Hausen, D.N. Halbe, E.U. Petersen and W.J. Tafuri (Editors), Salt Lake City, UT, pp. 389-396.

Mendoza, H. and Luraschi, A., 1993, "Impurity Elimination in Copper Converting", in *Converting, Fire Refining and Casting*, J.D. McCain and J.M. Floyd (Editors), TMS, San Francisco, CA, pp. 191-202.

Mendoza, H., Luraschi, A.A., Riveros, G.A., and Cerna, M.H., 1995, "Use of a Predictive Model for Impurity Behavior at the Chuquicamata Smelter", in *Copper 95-Cobre 95 International Conference*, Volume IV: Pyrometallurgy of Copper, A. Casali, G.S. Dobby, M. Molina and W.J. Thoburn (Editors), Metallurgical Society of CIM, Santiago, Chile, pp. 281-298.

Menzies, I.A., and Owen, L.W., 1966, "The Electrodeposition of Arsenic from Aqueous and Non-aqueous Solutions", *Electrochim. Acta,* 11, pp. 251-265.

Minería Chilena, Enero 2000, "Horno para Paipote".
Page web: http://www.editec.cl/mchilena/index.html

Minfact, 1995a, "Arsenic", No. 22, New South Wales Department of Mineral Resources.
Page web: http://www.minerals.nsw.gow.au

Minfact, 1995b, "Ottery Tin and Arsenic Mine", No. 39, New South Wales Department of Mineral Resources. Page web: http://www.minerals.nsw.gow.au

Mining Magazine, 1992, "Chilean Mining Projects", 171:4, pp. 202-207.

Ministère de l'Environnement, 1989, "Directive 019: Industries Minières", Gouvernement du Québec.

Ministerio de Minería de Chile, 1991, "*Decreto Ley N° 185: Funcionamiento de Establecimientos Emisores de Anhídrido Sulfuroso, Material Particulado y Arsénico en todo el Territorio Nacional*", Santiago, Chile.

Minoura, J., and Maeda, Y., 1984, "Current operation at Kosaka Smelter and Refinery", *Metallurgical Review of MMIJ,* 1:2, pp 138-156.

MIRAMAR, 2000, "Con Mine – Northwest Territories"
Page web: http://www.miramarmining.com/:

Mirza, A.H., Tahija, D., Chen, K., and Haung, H.H., 1988, "Formation and Stability Studies of Iron-arsenic and Copper-arsenic Compounds from Copper Electrorefining Sludge", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix, and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 37-58.

Mizanur, R., S., 1999, "Arsenic in Bangladesh Ground Water: The World's Greatest Arsenic Calamity".
Page web: http://www.dainichi-consul.co.jp/english/arsenic/article/mizanarticle.htm

Mohri, E. and Yamada, M., 1976, "Recovery of Metals from the Dusts of Flash Smelting Furnace", *in World Mining and Metal Technology,* Vol. 1, chapter 31, Proceedings of Joint MMIJ-AIME Meeting, Denver, CO, pp. 520-533.

Monhemius, A.J., and Swash, P.M., 1999, "Removing and Stabilizing As from Copper Refining Circuits by Hydrothermal Processing", *JOM,* 51:9, pp. 30-33.

More, M.A., and Pawson, H.E., 1978, "Giant Yellowknife Mines Limited", in *Mining Practice and Canada,* D. E. Pickett (Editor), CIM Special Volume 16, pp. 63-65.

Muñoz, G., 1996, "CODELCO-Chile's Corporate Decontamination Plan for its Smelters, in *EPD Congress '96,* G.W. Warren (Editor), TMS, Warrendale, PA, pp. 773-783.

Nadkarni, R.M., and Kusik, C.L., 1988, "Hydrometallurgical Removal of Arsenic from Copper Concentrates", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 263-286.

Nelson, F., and Kraus, K.A., 1955, "Anion Exchange Studies: Germanium and Arsenic in Hydrochloric Acid Solutions", *J. Am. Chem. Soc.,* 77, pp. 4508-4509.

Nenov, V., Dimitrova, N., and Dobrevsky, I., 1997, "Recovery of Sulphuric Acid from Waste Aqueous Solutions Containing Arsenic by Ion Exchange", *Hydrometallurgy,* 44, pp. 43-52.

Net Resources Int., 2000, "Kanowna Belle Gold Mine – Current Projects"
Page web: http://www.mining-technology.com/projects/kanowna/index.html

Nickson, R., McArthur, J., Burgess, W., Ahmed, K.M., Ravenscroft, P., and Rahman, M., 1998, "Arsenic Poisoning of Bangladesh Groundwater", *Nature,* 395, pp. 338.

Nishimura, T., Ito, C.T., Tozawa, K., and Robins, R.G., 1985, "The Calcium-Arsenic-Water-Air System", in *Impurity: Control and Disposal,* 15th Annual Hydrometallurgical Meeting, CIM, Vancouver, Canada, paper 2.

Nishimura, T., and Tozawa, K., 1985, "Removal of Arsenic from Waste Water by Addition of Calcium Hydroxide and Stabilization of Arsenic-Bearing Precipitates by Calcination", in *Impurity: Control and Disposal,* 15th Annual Hydrometallurgical Meeting, CIM, Vancouver, Canada, paper 3.

Nishimura, T., Itoh, C.T., and Tozawa, K., 1988, "Stabilities and Solubilities of Metal Arsenites and Arsenates in Water and Effect of Sulfate and Carbonate Ions on Their Solubilities", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 77-98.

Nishimura, T., and Robins, R.G., 2000, "Removal of Arsenic in Gold Cyanide Process", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 135-140.

Nishimura, T., Robins, R., and Twidwell, L.G., 2000, "The Removal of Arsenic from Hydrometallurgical Process and Effluents Streams", in *V International Conference on Clean Technology for the Mining Industry,* Vol. I: Waste Treatment and Environmental Impact in the Mining Industry, M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile.

Nishimura, T., and Umetsu, Y., 2000, "Chemistry on elimination of Arsenic, Antimony, and Selenium from Aqueous Solution with Iron (III) Species", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 105-112.

NIOSH, 1994a, "NIOSH Method 7300: Elements by ICP", in *NIOSH Manual of Analytical Methods (NMAM),* National Institute for Occupational Safety and Health, Fourth Edition. Page web: http://www.cdc.gov./niosh/pdfs/7300.pdf

NIOSH, 1994b, "NIOSH Method 5022: Arsenic, organo-", in *NIOSH Manual of Analytical Methods (NMAM),* National Institute for Occupational Safety and Health, Fourth Edition. Page web: http://www.cdc.gov./niosh/pdfs/5022.pdf

NORANDA, 1998, *Environment, Safety and Health Report.*
Page web: http://www.noranda.com/annual_rpts/environment_98/pdf/noreng.pdf

NORANDA, 1999, "Copper Operations: Altonorte Smelter"
Page web: http://www.noranda.ca/english/businesses/businesses.cfm?subsect_id=60&businesses=yes

Northern News Services, 2000, "Cleanup at $16.3 million: Report Says Arsenic Trioxide Solution Undecided", Yellowknife, updated 2000/01/12.
Page web: http://www.nnsl.com/frames/newspapers/archive00-1/jan00/jan12_00clean.html

O'kane, J., 1985, "Solvent Extraction Applied to Removal of Arsenic from Tankhouse electrolyte at Copper Refiniries Pty. Ltd.", in *Extraction Metallurgy '85,* A.G. Moncrieff (Editor), IMM, London, England, pp. 951-965.

Padilla, R., Fan, Y., Sanchez, M., and Wilkomirsky, I., 1998, "Processing High Arsenic Copper Concentrates", *IV International Conference on Clean Technology for the Mining Industry*. M. A. Sanchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 603-612.

Papassioni, N., Stefanakis, M., and Kontopoulos, A., 1988, "Removal of Arsenic from Solutions by Precipitation as Ferric Arsenates", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 321-334.

Parada, F., Ulloa, A., Carrasco, A., Wilkomirsky, I. and Jeraldo, L., "Desarsenification of Copper and Gold – Copper Concentrates in a Double Wall Pilot Fluid Bed Reactor", 1998, in *IV International Conference on Clean Technology for the Mining Industry*. M. A. Sanchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 613-621.

Pedreros, R., 1998, "Confinamiento de Residuos Arsenicales de Plantas de Acido", in *Primera Mesa Redonda Plantas de Acido,* Escuela de Ingeniería Química (Editor), Universidad Católica de Valparaiso, Viña del Mar, Chile.

Penman, D.W., 1985, "Metallurgical Aspects of the Treatment of Refractory Ores from Barberton", in *Impurity: Control and Disposal,* 15th Annual Hydrometallurgical Meeting, Vancouver, Canada, paper 8.

Pershagen, G., Wall, S., Taube, A., and Linnman, L., 1981, "On the Interaction Between Occupational Arsenic Exposure and Smoking and its Relationship to Lung Cancer", *Scand. J. Work Environ. Health*, 7, pp. 302-309.

Persson, H., Iwanic, M., El-Barnachawy, S., and Mackey, P.J., 1986, "The Noranda Process and Different Matte Grades, *JOM*, 38:9, pp. 34-37.

Pierce, M.L., and Moore, C.B., 1982, "Adsorption of Arsenite and Arsenate on Amorphous Iron Hydroxide", *Water Research,* 16, pp. 1247-1253.

Pinto, S.S., Henderson, V., and Enterline, P.E., 1978, "Mortality Experience of Arsenic-Exposed Workers", *Arch. Environ. Health*, 33, pp. 325-331.

Piret, N.L., and Melin, A.E., 1989, "An Engineering Approach to the Arsenic Problem in the Extraction of Non-Ferrous Metals", in *Proceedings of the International Symposium on Productivity and Technology in the Metallurgical Industries,* Koch, M. and Taylor, J.C. (Editors), TMS-AIME, Cologne, West Germany, pp. 735-814.

Piret, N. L., 1994, "Optimizing Bismuth Control during Copper Production", *JOM*, 46:10, pp. 15-18.

Piret, N.L., 1999, "Arsenic Management in Copper Smelting", in *Copper 99-Cobre 99*, Volume II: Mineral Processing/Environment, Health and Safety, B.A. Hancock and M.R.L. Pon (Editors), TMS, Phoenix, AZ, pp. 321-340.

Prasad, M.S., Mensah-Biney, R., and Pizarro, R.S., 1991, "Modern Trends in Gold Processing – Overview", *Mining Engineering*, 4:12, pp. 1257-1277.

Prater, J.D., Schlitt, W.J., and Richards, K.J., 1981, "Kennecott Process for Treating Copper Smelter Flue Dust", in *Process and Fundamental Considerations of Selected Hydrometallurgical Systems*, M. C. Kuhn (Editors), SME-AIME, New York, NY, pp. 126-141.

Qiankun, W., and Demopoulos, G.P., 1998, "A Novel Hydrometallurgical Process for the Immobilization of Arsenic", in *ICHM'98: Proceedings of the Third International Conference on Hydrometallurgy"*, Y. Xianwan, C. Qiyuan and H. Aiping (Editors), The Nonferrous Metals Society of China, Kunming, China, pp. 543-553.

Queirolo, C., 1998, "Future Development Strategy at Chuquicamata Smelter", in *IV International Conference on Clean Technology for the Mining Industry*. M. A. Sanchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile.

Reese, Jr., R. G., 1997, "Arsenic", *Minerals Yearbook*, U.S. Geological Survey. Page web: http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/160497.pdf

Reese, Jr., R. G., 1998, "Arsenic", *Minerals Yearbook*, U.S. Geological Survey. Page web: http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/160498.pdf

Reese, Jr., R. G., 1999, "Arsenic", U.S. Geological Survey, Mineral Commodity Summaries. Page web: http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/160399.pdf

Ritcey, G.M., and Ashbrook, A.W., 1981, "Treatment of Cobalt Arsenide Feeds for the Subsequent Recovery of Cobalt", *CIM Bulletin*, 74:834, pp. 103-112.

Robins, R.G., 1981, "The Solubility of Metal Arsenates", *Met. Trans. B*, 12, pp. 103-109.

Robins, R.G., 1982, "The Stabilities of Arsenic (V) and Arsenic (III) compounds in Aqueous Metal Extraction Systems", in *Hydrometallurgy, Research, Development and Plant Practice*, K. Osseo-Asare and J.D. Miller (Editors), TMS, Warrendale, PA, pp. 291-310.

Robins, R.G., and Tozawa, K., 1982, "Arsenic Removal from Gold Processing Waste Waters: The Potential Ineffectiveness of Lime", *CIM Bulletin*, 75:840, pp. 171-174.

Robins, R.G., 1984, "The Stability of Arsenic in Gold Mine Processing Wastes", in *Precious Metals: Mining, extraction and Processing*, AIME Annual Meeting, V. Kudryk, D.A. Corrigan and W.W. Liang (Editors), Los Angeles, CA, pp. 241-249.

Robins, R.G., 1985a, "The Aqueous Chemistry of Arsenic in Relation to Hydrometallurgical Processes", in *Impurity: Control and Disposal,* 15th Annual Hydrometallurgical Meeting, Vancouver, Canada, paper 1.

Robins, R.G., 1985b, "The solubility of Barium Arsenate: Sherritt's Barium Arsenate Process", *Met. Trans. B,* 16, pp. 404-406.

Robins, R.G., 1988, "Arsenic Hydrometallurgy", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 215-247.

Robins, R.G., Huang, J.C.Y., Nishimura, T., and Khoe, G.H., 1988, "The Adsorption of arsenate Ion by Ferric Hydroxide", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 99-112.

Robins, R.G., 1990, "The Stability and Solubility of Ferric Arsenate: An Update, in *EPD Congress '90,* D.R. Gaskell (Editor), TMS, Warrendale, PA, pp. 93-104.

Rojas, O.C., and Sanhueza, J.A., 1999, "Heman Videla Lira Copper Smelter Modernization", *Copper 99-Cobre 99 International Conference,* Volume V: Smelting Operations and Advances, D.B. George, W.J. Chen, P.J. Mackey and A.J. Weddick, (Editors), TMS, Phoenix, AZ, pp. 17-27.

Rojas, S., López, C., Roco, M., 1999, "Puesta en Marcha Planta de Acido Sulfúrico-Fundición Potrerillos", in *Segunda Mesa Redonda Plantas de Acido Sulfúrico,* Escuela Ingeniería Química (Editor), Universidad Católica de Valparaiso, La Serena, Chile.

Rojas, P., process engineer, Hemán Videla Lira (Paipote) smelter, private communication dated 2000/05/31.

Rondas, F., Scoyer, J., and Geenen, C., 1995, "Solvent Extraction of Arsenic with TPB – The Influence of High Iron Concentration on the Extraction Behaviour of Arsenic", in *Copper 95-Cobre 95 International Conference,* Volume III: Electrorefining and Hydrometallurgy of Copper, W.C. Copper, D.B. Dreisinger, J.E., Dutrizac, H. Hein, and U. Ugarte (Editors), Metallurgical Society of CIM, Santiago, Chile, pp. 325-335.

Rossovsky, S., 1993, "Process Development: Hydrometallurgical Treatment of Refractory Arsenical Gold Concentrates", *E&MJ,* June 1993, pp. 16FF-16HH.

Royston, D., and Hunter, T.C., 1983, "Solvent Extraction of Arsenic from Copper Tankhouse Electrolyte", paper A83-30, in *TMS/AIME Annual Meeting,* Atlanta, GA, pp. 1-11.

Sánchez, V.M., Castrejón, R., and Fontes, J.G., 1995, "Lixiviación Alcalina de los Polvos de Fundición de Cobre", in *XXI A.I.M.M.G. Meeting,* Acapulco, Mexico.

Sández, M., Mexicana de Cobre, S.A., private communication dated 2000/02/28.

Schlicher, R.J., and Ghosh, M.M., 1985, "Removal of Arsenic from Water by Physical Chemical Processes", *A. I. Ch. E. Symposium Series,* 81:243, pp. 152-164.

Shibata, T., Hashiuchi, M., and Kato, T., 1987, "Tomato Refinery's New Process for Removing Impurities from Electrolyte", in *The Electrorefining and Winning of Copper,* J.E. Hoffmann, et al. (Editors), Warrendale, PA, TMS-AIME, pp. 99-116.

Shuey, S., 1998, "São Bento: Eldorado's 1M-oz Brazilian Crown Jewel", *E&MJ,* October 1998, pp. 28-32.

SKS, 1998, "SKS Products Price", *Shui Kou Shan Mining Bureau.*
Page web: www.sksc.com/english/sks.htm

Smith, E.H., Foster, J.W., Minet, Ph., and Cauwe, Ph., 1985, "Selective Roasting to De-Arsenify Enargite/Pyrite Concentrate From St. Joe's El Indio Mine From Pilot Plant to Commercial Operation", in *Complex Sulfides,* A.D. Zunkel (Editor), TMS-AIME, Warrendale, PA, pp. 421-441.

Smith, E.H., 1986, "Metallurgy and Mineral Processing Plant at St. Joe's El Indio Mine in Chile", *Mining Engineering,* 38:10, pp. 971- 979.

Smith, E.H., and Paredes, E., 1988, "How St. Joe Gold's El Indio Mine Has Become a Major Producer of High Quality Crude Arsenic Trioxide", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 145-171.

Smith, A.H., Goycolea, M., Haque, R., and Biggs, M.L., 1998, "Marked increase in Bladder and Lung Cancer Mortality in a Region of Northern Chile due to Arsenic in Drinking Water", *Amer. J. Epidemiology,* 147:7, pp. 660-669.

Solozhenkin, P.M., Nebera, V.P., and Medvedeva-Lyalikova, N.N., 1999, "Transformation of Arsenic and tellurium in Solution by Fungi", in *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part B: Molecular Biology, Biosorption, Bioremediation, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, pp. 779-787.

Sracek, A., 1998, "Contaminación por Residuos Mineros", Seminario: *Aspectos Fenomenológicos e Hidrológicos en contaminación Ambiental,* Universidad Católica del Norte, Antofagasta, Chile.

Stefanakis, M., and Kontopoulos, A., 1988, "Production of Environmentally Acceptable Arsenites-Arsenates from Solid Arsenic Trioxide", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau, (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 287-304.

Stewart, C.L., Budac, J., Wrana, D., Krause, E., and Laundry, S.W., 1995, "Development of a Copper Arsenate Process for Inco's Manitoba Division", *CIM Bulletin,* 88:998, pp. 117-123.

Swash, P.M. and Monhemius, A.J., 1994, "The Hydrothermal Precipitation from Aqueous Solutions Containing Iron(III), Arsenate and Sulfate", in *Hydrometallurgy 94,* Proceedings of Conference in Cambridge, UK, IMM, Chapman and Hall, pp. 177-190.

Swash, P.M. and Monhemius, A.J., 1998, "The Scodorite Process: A Technology for the Disposal of Arsenic in the 21st Century", in *Effluent Treatment in the Mining Industry,* Chapter 3, M. A. Sánchez, F. Vergara, and S.H. Castro (Editors), University of Concepción, Chile, pp. 119-161.

Szilassy, I., and Vadasdi, 1990, "Solvent Extraction of Arsenic from Sodium Tungstane Solutions", in *Solvent Extraction 1990,* Proceedings of the International Solvent Extraction Conference (ISEC'90), Part B, Process Metallurgy 7B, T. Sekine (Editor), pp. 1139-1144.

Tahija, D., and Huang, H.H., 2000, "Factors Influencing Arsenic Coprecipitation with Ferric Hydroxide", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 149-156.

Takagi, R., and Yabe, K., 1956, "Recovery of Selenium and Arsenic from Aqueous Solutions of Selenium Solutions Compounds Containing Arsenic Compounds by Electrolytic Reduction", *Japan Patent 6602.*

Takahashi, M., Ito, E., and Nagai, T., "Method for Removing Arsenic from Copper Electrolytic Solutions or the Like", *Canadian Patent: 1,070,504,* July 1980.

Terayama, T, Sumitomo Metal Mining, "Arsenic Recovery and High Purity Arsenic Metal Production from Arsenic Residues of Copper Smelting Process", private communication dated 1999/06/09.

Terry, B.S., 1992, "Arsenic Control in Hydrometallurgy and Pyrometallurgy", in *I International Conference on Clean Technology for the Mining Industry,* M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 93-99.

Tomita, M., Higashi, M., Oto, S., and Okamoto, H., 1991, "Hydrometallurgical Process of Copper converter Dust at the Saganoseki Smelter & Refinery", in *Residues and Effluents – Processing and Environmental Considerations,* R.G. Reddy, W.P. Imrie and P.B. Queneau (Editors), TMS, San Diego, CA, pp. 282-293.

Torres, I.E., and Doan, D.D., 1997, "The Ministry Industry of Mexico", U.S. Geological Survey. Page web: http://minerals.usgs.gov/minerals/pubs/country/9516097.pdf

Totsuka, T., Sasaki, K., and Nagai, T., 1986, "Fundamental Studies on Purification of Copper Electrolyte", *Metallurgical Review of MMIJ,* 3:2, pp. 146-158.

Toyabe, K., Segawa, C., and Sato, H., 1987, "Impurity Control of Electrolyte at Somitomo Niihama Copper", in *The Electrorefining and Winning of Copper,* J.E. Hoffmann, et al. (Editors), Warrendale, PA, TMS-AIME, pp. 117-128.

Toyabe, K., Segawa, C., Kadoya, H., and Ohwa, H., 1988, "High Purity Arsenic Metal Production at SMM's Nihama Copper Refinery", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 351-362.

Tozawa, K., Nishimura, T., and Umetsu, Y., 1977, "Removal of Arsenic from Aqueous Solutions", in *16th CIM Conference Metallurgists,* Vancouver, Canada.

Tozawa, K., Nishimura, T., Umetsu, Y., 1978, "Hydrometallurgical Recovery or Removal of Arsenic from Copper Smelter by-products", *107th AIME Meeting,* Denver, CO.

Tozawa, K., and Nishimura, T., 1984, "Oxidation of As (III) to As (V) in Aqueous Solutions", *Metall. Review MMIJ,* 1:1, pp. 76-87.

Tserekova, A.M., et al., 1970, "Tributyl Phosphate Extraction of Arsenic (V) from Sulfuric Acid Solutions", *Sb. Nauch. Tr., Vses. Nauch. – Issled. Gornomet. Inst. Tsvet. Metal.,* 19, pp. 119-124.

Twidwell, L.G., Plessas, K.O., Comba, P.G., and Dahnke, D.R., 1995, "Removal of Arsenic from Wastewaters and Stabilization of Arsenic Bearing Waste Solids: Summary of Experimental Studies", *Min. Process. Extractive Metall. Review,* 15, pp. 237-246.

US EPA, 1990, "Sec. 112: National Emission Standards for Hazardous Air Polluants", in *Clean Air Act,* Title I: Air Pollution Prevention and Control, Part A: Air Quality and Emission limitation". Page web: http://www.epa.gov/oar/caa/caa112.txt

US EPA Journal, 1991, "Highlights of the 1990 Clean Air Act Amendments: Air Toxics", *History Office.* Page web: http://www.epa.gov/history/topics/caa90/01.htm

US EPA, 1998a, "Locating and Estimating Air Emissions from Sources of Arsenic and Arsenic Compounds", *Report No. EPA-454/R-98-013,* US Environmental Protection Agency, Office of Air Quality. Page web: http://www.epa.gov/ttnchie1/efdocs/arsnic_1.pdf

US EPA, 1998b, *Test Methods for Evaluating Solid Waste: Physical /Chemical Methods,* SW-846 On-line, US Environmental Protection Agency, Office of Solid Waste.
Page web: http://www.epa.gov/epaoswer/hazwaste/test/7xxx.htm

US EPA, 1998c, "Rule and Implementation Information for Primary Copper Smelters", Environmental Protection Agency, Office of Air Quality, Planning & Standards (OAQPS).
Page web: http://www.epa.gov/ttnuatw1/copper/copperpg.html

USGS, 1999, "Arsenic", in *Metal Prices in the United States Through 1998*, pp. 7-8.
Page web: http://minerals.usgs.gov/minerals/pubs/metal_prices/metal_prices1998.pdf

Valenzuela, P., CONAMA Chile, IV region, private communication dated 1999/03/09.

Van Weert, G., and Droppert, D., 1994, "Aqueous Processing of Arsenic Trioxide to Crystalline Scorodite", *JOM*, 46:6, pp. 36-38.

Vega, D., smelter engineer, Caletones smelter, private communication dated 2000/05/16.

Velasco, P., 1996, "The Mineral Industry of Chile", *Minerals Yearbook*, U.S. Department of the Interior, U.S. Geological Survey, Minerals Information.
Page web: http://minerals.er.usgs.gov/minerals/pubs/country/9506096.pdf.

Velasco, P., 1997a, "The Mineral Industry of Bolivia", U.S. Geological Survey.
Page web: http://minerals.usgs.gov/minerals/pubs/country/9503097.pdf

Velasco, P., 1997b, "The Mineral Industry of Chile", U.S. Geological Survey.
Page web: http://minerals.usgs.gov/minerals/pubs/country/9506097.pdf

Vircikova, E., and Imriš, I., 1995, "Arsenic Distribution in Copper Smelter and an Environmentally Friendly Way to Remove it", in *Copper 95-Cobre 95 International Conference*, Volume II: Mineral Processing and Environment, A. Casali, G.S. Dobby, M. Molina and W.J. Thoburn (Editors), Metallurgical Society of CIM, Santiago, Chile, pp. 422-450.

Vircikova, E., and Palfy, P., 1998, "Arsenic Abatement from Smelter Gases", in *Effluent Treatment in the Mining Industry,* M. A. Sanchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 163-231.

Vircikova, E., and Havlik, M., 1999, "Removing As from Converter Dust by a Hydrometallurgical Method", *JOM*, 51:9, pp. 20-23.

Vuskovic, J., 1996, "Revisión de Parámetros Operacionales de la Planta de Tratamiento de Polvos de Fundición, Tesis Ingeniero de Ejecución en Metalurgia, Universidad de Atacama, Copiapó, Chile.

Wall, S., 1980, "Survival and Mortality Pattern Among Swedish Smelter Workers", *Int. J. Epidemiol.*, 9, pp. 73-87.

Weir, D.R., and Master, I.M., 1980, "Removal of Arsenic from Aqueous Solutions", *Canadian Patent, 358,966.*

Weisenberg, I. J., Bakshi, P.S., and Vervaert, A.E., 1979, "Arsenic Distribution and Control in Copper Smelters", *JOM*, 30:10, pp. 38-44.

Welch, K., Higgins, I., Oh, M., and Burchfiel, C., 1982, "Arsenic Exposure, Smoking, and Respiratory Cancer in Copper Smelter Workers", *Arch. Environ. Health*, 37, pp. 325-335.

White, T., and Toor, I., 1996, "Stabilizing Toxic Metal Concentrates by Using SMITE", *JOM*, 48:3, pp. 54-57.

WHO, 1981, "Arsenic", *Environmental Health Criteria*, N° 18, Geneva: World Health Organization.

Wicks, M.J., Archer, V.E., Auerbach, O., and Kuschner, M., 1981, "Arsenic Exposure in a Copper Smelter as Related to Histological Type of Lung Cancer", *Am. J. Ind. Med.*, 2, pp. 25-31.

Wiertz, J.V., and Rozas, I., 1996, "Technological Alternatives for the Reduction of Arsenic Emission in Chilean Copper Smelters", *III International Conference on Clean Technology for the Mining Industry*. M. A. Sanchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 289-297.

Wiertz, J.V., and Gutierrez, M., 1998, "Arsenic Management and Disposal in the Chilean Copper Industry", *IV International Conference on Clean Technology for the Mining Industry*. M. A. Sanchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 593-602.

Wilson, R., 1998, "Chronic Effects of Arsenic on Human Health", *Harvard Arsenic Project*. Page web: http://phys4.harvard.edu/~wilson/arsenic_project_effects.html

World Bank, 1998, "Copper Smelting", in *Pollution Prevention and Abatement Handbook*, World Bank Group", pp. 291-294.
Page web: http://wbln0018.worldbank.org/essd/essd.nsf/GlobalView/PPAH/$File/54_coppr.pdf

Wu, J.C., U.S. Geological Survey, private communication dated 1999/05/24.

Xuewen, W., Ziping, L., Zhongfu,, S., Qinyi, L., Ben, Z., and Yan, L., 1998, "Adsorption of Impurities in Copper Electrolity Onto Silver Extracted Residue of Copper Anode Slime", in *ICHM'98: Proceedings of the Third International Conference on Hydrometallurgy"*, Y. Xianwan, C. Qiyuan and H. Aiping (Editors), The Nonferrous Metals Society of China, Kunming, China, pp. 660-662.

Zaldivar, R., 1980, "A Morbid Condition Involving Cardio-vascular, Broncho-pulmonary, Digestive and Neural Lesions in Children and Young Adults After Dietary Arsenic Exposure", *Zentralbl. Bakteriol.*, I. Abt. Orig. B, 170:44.

Zeping, Y., 1999, "Distribution and Removal of Impurities in Copper Smelting in Guixi Smelter", in *Copper 99-Cobre 99*, Volume V: Smelting Operations and Advances, D.B. George, W.J. Chen, P.J. Mackey and A.J. Weddick (Editors), TMS, Phoenix, AZ, pp. 345-355.

APPENDIX I: BIBLIOGRAPHY

1. ARSENIC AND ITS COMPOUNDS

1.1 Physical and Chemical Nature

Allen, V.T., and Fahey, J.J., 1948, "Mansfieldite, a New Arsenate, the Aluminium Analogue of Scorodite and the Mansfieldite-scorodite series, *American Mineralogist,* 33, pp. 122-133.

Ballantyne, J.M., and Morre, J.N., 1988, "Arsenic Geochemistry in Geothermal Systems", *Geochem. Cosmo. Acta,* 52, pp. 475-483.

Belkin, H.E., Zheng, B., Zhou, D., and Finkelman, R.B., 1997, "Preliminary Results on the Geochemistry and Mineralogy of Arsenic in Mineralized Coals from Endemic Arsenosis Areas in Guizhou Province, P.R. China, in *Proceedings, Fourteenth Annual International Pittsburgh Coal Conference & Workshop,* Taiyuan, Shanxi, People's Republic of China, pp. 1-20.
Abstract on line: http://www.dainichi-consul.co.jp/english/arsenic/belkin.htm

Boyle, R.W., and Jonasson, I.R., 1973, "The Geochemistry of Arsenic and its Use as a Indicator Element in Geochemical Prospecting", *J. Geochem. Exploration*, 2, pp. 251-296.

Crecelius, E.A., Bothner, M.H., and Carperta, R., 1975, "Geochemistries of Arsenic, Antimony, Mercury and Related Elements in Sediments of Puget Sound", *Environ. Sci. Technol.,* 9, pp. 323-333.

Cullen, W.R., and Reimer, K.J., 1989, "Arsenic Speciation in the Environment, *Chem. Rev.,* 89, pp. 713-764.

De Vitre, R., Belzile, N., and Tessier, A., 1991, "Speciation and Adsorption of Arsenic on Diagenetic Iron Oxyhydroxydes", *Limnol. Oceanogr.,* 36:7, pp. 1480-1485.

Evans, L.J., 1989, "Chemistry of Metal Retention by Soils", *Environ. Sci. Technol.,* 23, pp. 1046-1056.

Faust, S.D., Winka, A.J., and Belton, T., 1987, "An Assessment of Chemical and Biological Significance of Arsenical Species in the Maurice River Drainage Bassin", *Journal of Environmental Science and Health,* A22, pp. 239-262.

Goyer, N., 1980, *Vue d'ensemble sur les Substances Toxiques: Arsenic*, Environnement Québec, 33p.

Hadni, R.D., 2000, "The Mineralogy of Minor and Trace Elements in the Co-Ni-Cu-Pb-Zn Ores of the Viburnum Trend, Southeast Missouri: Ag, Cd, Ge, Co, Ni, As, Sb, and Bi Minerals", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi*, C. Young (Editor), SME, Littleton, Co, USA, pp. 181-190.

Lynch, D.C., 1988, "A Review of the Physical Chemistry of Arsenic as it Permains to Primary Metals Production", in *Arsenic Metallurgy Fundamentals and Applications*, Reddy, R.G., Hendrix, J.L., and Queneau, P.B. (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 3-33.

Onishi, H., 1969, "Arsenic 33", in *Handbook of Geochemistry*, K.H. Wedepohl (Editor), Springer-Verlag, New York.

Onishi, H., and Sandell, E.B., 1955, "Geochemistry of Arsenic", *Geochim. et Cosmochimica Acta*, 7, pp. 1-33.

Polmear, I.J., 1998, "Metallurgy of the Elements", in *Chemistry of Arsenic, Antimony, and Bismuth*, N.C. Norman (Editor), School of Chemistry, University of Bristol, Bristol, UK, Blakie Academic & Professional, pp. 39-65.

1.2 Arsenic in the Environment

Acharyya, S.K., "Arsenic in Groundwater - Geological Overview", 1997, in *Consultation on Arsenic in Drinking Water and Resulting Arsenic Toxicity in India and Bangladesh*, WHO, New Delhi, India.

Aggett, J., 1988, "Current Understanding of the Arsenic Cycle in Waikato Hydro-lakes: Traces Elements in New Zealand: Environmental, Human and Animal", in *Proceeding NZ Trace Elements Group Conference*, Lincoln College, Canterbury, New Zealand.

Aggett, J., and O'Brien, G.A., 1985, "Detailed Model for the Mobility of Arsenic in Lacustrine Sediments Based on Measurements in Lake Ohakuri", *Environ. Sci. Technol.*, 19, pp. 231-238.

Anderson, L. C. D., and Bruland, K. W., 1991, "Biogeochemistry of Arsenic in Natural Waters: the Importance of Methylated Species", *Environ. Sci. & Tech.*, 25, pp. 420-427.

Andreae, M.O., 1978, "Distribution and Speciation of Arsenic in Natural Waters and Some Marine Algae", *Deep-sea Res.*, 25, pp. 391-402.

Arsenic in Mine Tailings: Questions and Answers, Public Health Division, Department of Human Services, Melbourne, Victoria, Australia, March 1998.
Page web: http://hna.ffh.vic.gov.au/phb/hprot/env_htth/tailings/index.htm

Azcue, J.M., Mudroch, A., Rosa, F., and Hall, G.E.M., 1994, "Effects of Abandoned Gold Mine Tailings on the Arsenic Concentration in Water and Sediments of Jack of Clubs Lake, B.C.", *Environmental Technology,* 15, pp. 669-678.

Ballantyne, J.M. and Moore, J.N., 1988, "Arsenic Geochemistry in Geothermal Systems", *Geochim. Cosmochim. Acta,* 52, pp. 475-483.

Bhumbla, D.K., and Keefer, R.F., 1994, "Arsenic Mobilization and Bioavailability in Soils", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 51-83.

Braman, R.S., 1975, "Arsenic in the Environment", in *Arsenical Pesticides,* American Chemical Society, Washington, DC, pp. 108-123.

Brannon, J.M., and Patrick, W.H., 1987, "Fixation, Transformation and Mobilization of Arsenic in Sediments", *Environ. Sci. & Tech.,* 21, pp. 450-459.

Bowell, R.J., 1994, "Sorption of Arsenic by Iron Oxides and Oxyhydroxides in Soils", *Appl. Geochem.,* 9, pp. 279-286.

Bowell, R.J., Morley, N.H., and Din, V.K., 1994, "Arsenic Speciation in Soil Porewaters from the Ashanti Mine, Ghana", *Appl. Geochem.,* 9, pp. 15-22.

Cassity, W.D., and Pesic, P., 1995, "Interaction of *Thiobacillus Ferroxydans* with Arsenite, Arsenate and Arsenopyrite, in *New Remediation Technology in the Changing Environmental Arena,* Society for Mining, Metallurgy and Exploration, Littleon, CO, pp. 223-228.

Cherry, J.A., Shaikh, A.U., Tallman, D.E., and Nicholson, R.V., 1979, "Arsenic Species as an Indicator of Redox Conditions in Groundwater, *J. of Hydrology,* 43, pp. 379-392.

Chunguo, C., and Zihui, L., 1988, "Chemical Speciation and Distribution of Arsenic in Water, Suspended Solids and Sediments of Xiangjiang river, China", *Science Total Environ.,* 77, pp. 69-82.

Clayton, J.S., and Tanner, C.C., 1994, "Environmental Persistence and Fate of Arsenic Applied for Aquatic Weed Control", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 345-363.

Clement, W.H., and Faust, S.D., 1981, "The release of Arsenic from Contaminated Sediments and Muds", *J. Environ. Sci. Health,* A16, pp. 87-122.

Chilvers, D.C. and Peterson, P.J., 1987, "Global cycling of Arsenic", in *Lead, Mercury, Cadmium and Arsenic in the Environment,* ed. Hutchinson, T.C. and Meema, K.M., Scientific Committee on Problems of the Environment (SCOPE 31), Wiley, New York.

Das, D., Samanta, G., Mandal, B.K., Chowdhury, T.R., Chanda, C.R., Chowdhury, P.P., Basu, G., and Chakraborti, D., 1997, "Arsenic in Groundwater in Six Districts of West Bengal", in *Consultation on Arsenic in Drinking Water and Resulting Arsenic Toxicity in India and Bangladesh,* WHO, New Delhi, India.

Ferguson, J.F., and Davis, J., 1972, "A Review of the Arsenic Cycle in Natural Waters, *Water Research,* 6, pp. 1259-1274.

Francesconi, K.A., and Edmonds, J.S., 1994, "Biotransformation of Arsenic in the Marine Environment", in *Arsenic in the Environment, Part I: Cycling and Characterization,* J.O. Nriagu (Editor), Wiley, New York, pp. 221-261.

Freeman, M.C., 1985, "The Reduction of Arsenate to Arsenite by *an .Anabaena Oscillaroides*-bacteria Assemblages Isolated from the Waikato River", *J. Marine Freshwater Resources,* 19, pp. 277-282.

FuHua, C., KeLian, Y., and ShuGui, D., 1994, "Distribution and Transformation of Arsenic in the Southern Drainage Canal of Tianjin City", in *Arsenic in the Environment, Part I: Cycling and Characterization,* J.O. Nriagu (Editor), Wiley, New York, pp. 337-344.

Hanford, C.A., Hering, J.G., and Chiu, V.Q., 1997, "Arsenic Occurrence and Speciation in Groundwater: Implications for Health Effects and Treatment Options", in *CSCE/ASCE Environmental Engineering Conference,* Edmonton, Canada.

Kabata-Pendias, A., and Pendias, H., 1992, *Trace in Soils and Plants,* 2nd Edition, CRC Press, 365p.

Karim, M. M., Komori, Y., Alam, M., 1997, "Subsurface Arsenic Occurrence and Depth of Contamination in Bangladesh", *J. of Environ. Chem.,* 7:4, pp. 783-193. Abstract on line: http://www.dainichi-consul.co.jp/english/pub/JECpap1.htm

Kavanagh, P.J., Farago, M.E., Thornton, L., and Braman, R.S., 1997, "Bioavailability of Arsenic in Soil and Mine Wastes of the Tamar Valley, S-W England", *Chemical Speciation Bioavailability,* 9:3, pp. 77-82.

Ladeira, A.C.Q., and Ciminelli, V.S.T., 2000, "Mobility of As (III) and As (V) Soils", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, Co, USA, pp. 191-198.

Lead, Mercury, Cadmium and Arsenic in the Environment, T.C. Hutchinson and K.M. Meena (Editors), Wiley, New York, 1987.

Lunde, G., 1973, "The Synthesis of Fat and Water Soluble Arseno Organic Compounds in Marine and Limnetic Algae", *Acta Chem. Scand.,* 27, pp. 1586-1594.

Maeda, S., 1994, "Biotransformation of Arsenic in the Freshwater Environment", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 155-188.

McLaren, S.J., and Kim, N.D., 1994, "Evidence for a Seasonal Fluctuation of Arsenic in New-Zealand Longest River and the Effect of Treatment on Concentration in Drinking Water", *Environ. Pollution,* 90:1, pp. 67-73.

Mok, W.M., and Wai, C.M., 1989, "Distribution and Mobilization of Arsenic Species in the Blackbird Mining Area, Idaho", *Water Resources,* 23, pp. 7-13.

Mok, W.M., and Wai, C.M., 1990, "Distribution and Mobilization of Arsenic and Antimony Species in the Cœur D'Alène River System, Idaho", *Environ. Sci. Technol.,* 24, pp. 102-108.

Mok, W.M., and Wai, C.M., 1994, "Mobilization of Arsenic in Contaminated River Waters", in *Arsenic in the Environment, Part I: Cycling and Characterization,* J.O. Nriagu (Editor), Wiley, New York, pp. 99-118.

Moore, J.N., Ficklin, W.H., and Johns, C., 1988, "Partitionning of Arsenic and Metals in Reducing Sulfidic Sediments", *Enviorn. Sci. Technol.,* 22, pp. 432-437.

Mushtaq, A., 1998, "Arsenic in Soil and Water of Bangladesh: A Scientific Report", OEAD, Austria, p. 1-10.

O'Neill, P., 1990, "Arsenic", in *Heavy Metals in Soils,* B.J. Alloway (Editor), Chapter 5, Blackie, Glasgow, UK, pp. 83-99

Oscarson, D.W., Huang, P.M., Defosse, C., and Herbillon, A., 1981, "Oxidative Power of Mn (IV) and Fe (III) Oxides with Respect to As (III) in Terrestrial and Aquatic Environments", *Nature,* 291, pp. 50-51.

Otte, M.L., and Ernst, W.H.O., 1994, "Arsenic in Vegetation of Wetlands", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 365-379.

Parris, G.E., and Brinckman, F.E., 1976, "Reactions which Relate to environmental Mobility of Arsenic and Antimony", *Environ. Sci. Technol.,* 10, pp. 1128-1134.

Phillips, D.J.H., 1994, "The Chemical Forms of Arsenic in Aquatic Organisms and Their Interrelationships", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 262-288.

Reimer, K.J., and Thompson, J.A.J., 1988, "Arsenic Speciation in Marine Interstitial Water", *Biogeochem.*, 6, pp. 211-237.

Richarson, V.W., and Vaughan, J.D., 1978, "Arsenic Concentrations in Surface Runoff from Small Watersheds in Texas", *J. Environ. Qual.*, 7, pp. 189-192.

Robertson, F.N., 1989, "Arsenic in Groundwater Under Oxidizing Conditions, Southwest United States", *Environmental Geochemistry and Health*, 11, pp. 171-185.

Roussel, C., Bril, H., and Fernandez, A., 2000, "Arsenic Speciation: Involvement in Evaluation of Environmental Impact Caused by Mine Wastes", *J. Environ. Qual.*, 29, pp. 182-188.

Sancha, A.M. (Editor), "Arsenic in the Environment and its Incidence on Health", *International Seminar Proceedings,* University of Chile, Santiago, Chile, 1994.

Sanders, J.G., Riedel, G.F., and Osman, R.W., 1994, "Arsenic Cycling and Its Impact in Estuarine and Coastal Marine Ecosystems", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 289-308.

Schaufelberger, F.A., 1994, "Arsenic Minerals Formed at Low Temperatures", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 403-415.

Servant, J., 1982, *Atmospheric Trace Elements from Natural and Industrial Sources,* Monitoring and Assessment Research Centre, N° 27, 37p.

Shotyk, W., 1994, "Natural and Anthropogenic Enrichments of Arsenic Through Three Canadian Ombrotrophic *Sphagnum* Bog Profiles", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 381-401.

Silvarama, K. 1994, "Treatment of Anaconda Smelter Site Soil for Arsenic Removal", *M. Sc. Thesis,* Montana Tech College Min. Sci. Tech., Butte, MT, USA.

Smedley, P.L., 1997, "Arsenic in Groundwater in Bangladesh", in *Consultation on Arsenic in Drinking Water and Resulting Arsenic Toxicity in India and Bangladesh,* WHO, New Delhi, India.

Tremblay, G-H., and Gobeil, C., 1990, "Dissolved Arsenic in the St. Lawrence Estuary and the Saguenay Fjord", *Canada Maritime Pollution Bull.*, 21, pp. 465-469.

US EPA, 1994, "Superfund at Work: Hazardous Waste Cleanup Efforts Nationwide", Report: EPA-520/F-94-008, Solid Waste and Emergency Reponse".
Page web: http://es.epa.gov/oeca/spfund/epa520-f-94-008.pdf

Wakao, N., Koyatsu, H., Komai, Y., Shimokarawa, H., Sakurai, Y., and Shiota, H., 1988, "Microbial Oxidation of Arsenite and Occurrence of Arsenite-oxidizing Bacteria in Acid Mine Water from a Sulfur-pyrite Mine", *Geomicrobiology J.*, 6, pp. 11-24.

Welch, A.H., Lico, M.S., and Hughes, J.L., 1988, "Arsenic in Ground Water of the Western United States", *Ground Water*, 26:3, pp. 333-347.

Wood, J.M., 1974, "Biological Cycles for Toxic Elements in the Environment", *Science*, 183 (March), pp. 1049-1052.

Xiankun, L., Jing, L., and Xinian, M., 1994, "Arsenic in Several Chinese Estuaries and Coastal Seas", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 309-336.

Xu, H., Allard, B., and Grimwall, A., 1988, "Influence of pH and Organic Substance on the Absorption of As(V) on Geologic Materials", *Water, Air, Soil Pollution*, 40, pp. 293-305.

Xu, H., Allard, B., and Grimwall, A., 1991, "Effects of Acidification and Natural Organic Materials on the Mobility of Arsenic in the Environment", *Water, Air, Soil Pollution*, 57-58, pp. 269-278.

Yan-Chu, H., 1994, "Arsenic Distribution in Soils", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 17-49.

Yang, J.R., 1986, "Accumulation and Transport of Arsenic in Soil", *Huanjing Kexue*, 7:2, pp. 26-31.

1.3 Arsenic and Human Health

AIIH&PH, 1997, "Arsenic Contamination of Groundwater and Its Remedial Action Plan in West Bengal", in: *Consultation on Arsenic in Drinking Water and Resulting Arsenic Toxicity in India and Bangladesh*, WHO, New Delhi, India.

Arsenic Calamity of Bangladesh, Dainichi Consultant Page Web, Gifu, Japan.
Page web: http://www.dainichi-consul.co.jp/english/arsenic/arsarticles.htm

Arsenic: Exposure and Health, Chappel, W. R., Abernathy, C. O., and Cothern, C. R. (Editors), *Special Issue of Environmental Geochemistry and Health*, 16, Science and Technology Letters, Northwood, 1994.

Arsenic: Industrial, Biomedical, Environmental Perspectives, W.H. Lederer and R.J. Fensterheim (Editors), Van Nostrand Reinhold, New York, 1984.

Arsenic in Drinking Water, Subcommitte on Arsenic in Drinking Water, National Research Council, U.S.A., 330 pages, 1999.
Available on line: http://books.nap.edu/books/0309063337/html/90.html#pagetop

Arsenic in the Environment, Part II: Human Health and Ecosystem Effects. J.O. Nriagu (Editor), Wiley, New York, 1994.

Biological and Environmental Effects of Arsenic, B.A. Fowler (Editor), Elsevier, Amsterdam, 1983.

Cebrian, M.E., Albores, A., Aguilar, M., and Blakely, E., 1983, "Chronic Arsenic Poisoning in the North of Mexico", *Human Toxicology*, 2, pp. 121-133.

Crecelius, E.A., Johnson, C.J., and Hofer, G.C., 1974, "Contamination of soils Near a Copper Smelter by Arsenic, Antimony and Lead", *Water, Air, Soil Pollution,* 3, pp. 337-342.

Habashi, F., and Ismail, M.I., 1975, "Health Hazards and Pollution in the Metallurgical Industry due to Phosphine and Arsine", *CIM Bulletin,* 68:760, pp. 99-103.

Hertz-Picciotto, I., Arrighi, H.M., and Hu, S., 2000, "Does Arsenic Exposure Increase the Risk for Circulatory Disease?", *American J. Epidemiology,* 151:2, pp. 174-181.

Hussam, A., Alauddin, M., Khan, A.H., Rasul, S.B., and Munir, K.M., 1999, "Evaluation of Arsine Generation in Arsenic Field Kit", *Environ. Sci. Technol.,* 33, pp. 3686-3688.

Institute of Engineer's Dhaka, *Seminar on Arsenic Problem in Drinking Water of Bangladesh,* Dhaka, 30 October 1996.

Karim, M.M., "Arsenic in Groundwater and Health Problems in Bangladesh", *J. Water Research (in press).* Abstract on line: http://www.dainichi-consul.co.jp/english/pub/pas2.htm

Karim, M.M., and Begum, Z.R., 1999, "Groundwater Arsenic Contamination Inventories and Risk Assessment using Geographic Information System: Case Studies Kishoreganj and Netrokona District of Bangladesh", *in 92nd Annual Meeting of A&WMA*, San Diego, St. Louis.
Abstract on line: http://www.dainichi-consul.co.jp/english/pub/awma99.htm

Luh, M. D., Baker, R. A., and Henley, D. E, 1973, "Arsenic Analysis and Toxicity – a Review", *Science Total Environ.*, 2:1, pp. 1-12.

Manz, M., and Castro, J., 1997, "The Environmental Hazard Caused by Smelter Slags From the Sta. María de la Paz Mining District of Mexico", *Environmental Pollution,* 98:1, pp. 7-13.

Mazumder, D.N.G., Das Gupta, J., Santra, A., Pal, A., Ghose, A., Sarkar, S., Chattopadhaya, N., and Chakraborti, D., 1997, "Non-cancer Effects of Chronic Arsenicosis with Special Reference to Liver Damage", in *Arsenic:Exposure and Health Effects*, C.O. Abernathy, R.L. Calderon and W.R. Chappell (Editors), Chapman & Hall, Chapter 10, pp. 112-123.

Mushtaq, A., Brandstetter, A., Wenzel, W., and Winfried, E.H., 1997, "The Arsenic Calamity in Bangladesh", in *Proceeding of 4th International conference on the Biogeochemistry of Trace Elements*, Berkeley, California, pp. 263-264.

Mushtaq, A., 1999, "Environmental Impact of Arsenic in Austria and Bangladesh: Its Distribution and Fractionation in Relation to Soil Properties", *Ph.D. Thesis*, Institute of Soil Research, University of Agriculture, Vienna, Austria, p. 1-190.

Nordstrom, D.K., 2000, "An Overview of Arsenic Mass-Poisoning in Bangladesh and West Bengal, India", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, Co, USA, pp. 21-30.

NRCC, 1978, "General Arsenic Toxicity", in *Effects of Arsenic in the Canadian Environment,* National Research Council Canada, Ottawa.

Rahman, M., and Axelson, O., 1995, "Diabetes Mellitus and Arsenic Exposure: a Second Look at Case-control Data from a Swedish Copper Smelter", *Occupational & Environmental Medicine*, 52, pp. 773-774.

Rahman, M., Wingren, G., and Axelson, O., 1995, "Diabetes Mellitus Among Swedish Art Glass Workers - an Effect of Arsenic Exposure?", *Scandinavian J. Work Environ. Health*, 22, pp. 146-149.

Rahman, M., Tondel, M., Ahmad, S.A., and Axelson, O., 1998, "Diabetes Mellitus Associated With Arsenic Exposure in Bangladesh", *American J. Epidemiology,* 148:2, pp. 198-203.

Ratan K.D., Bhajan Kr.B., Gautam, S., Badal, Kr.M., Chakraborti, D., Shibtosh, R., Abu, J., Ariful, I., Gulshan, A., Saiful, K.A., Wadud, K., Akther, A., and Abdul, H., 1997, "Groundwater Arsenic Calamity in Bangladesh", *Current Science*, 73:1, pp. 48-59.

Smith, A., 1997, "Experiences with Large Scale Arsenic Toxicity in Other Parts of the World", in *Consultation on Arsenic in Drinking Water & Resulting Arsenic Toxicity in India and Bangladesh*, WHO, New Delhi, India.

Tam, G.K.H., Charbonneau, S.M., Bryce, F., Pomroy, C., and Sandi, E., 1979, "Metabolism of Inorganic Arsenic in Humans following Oral Ingestion", *Toxicol. Appl. Pharmacol,* 50, pp. 319-322.

Tondel, M., and Rahman, M., 1998, "Arsenic Poisoning in Bangladesh - The Largest Disaster in Our Time?", *Folkh Sovetenskapligt Centrum Nyhetsblad*, 8, (Swedish).

Tseng, W.P., Chu, H.M., How, S.W., Fong, J.M., Lin, C.S., and Yeh, S., 1968, "Prevalance of Skin Cancer in an Endemic Area of Chronic Arsenicism in Taiwan", *J. of the National Cancer Institute*, 40:3, pp. 453-463.

US EPA, 1985, "Health Assessment Document for Inorganic Arsenic", U.S. Environmental Protection Agency, EPA-600/S8-83/021F, Washington, DC.

US EPA, 1988, "Special Report on Ingested Inorganic Arsenic - Skin Cancer, Nutritional Essentiality", US Environmental Protection Agency, EPA-625/3-87-013. Washington, DC.

US EPA, 1998, "Arsenic and Compounds", *Unified Air toxics Website,* Office of air Quality, Planning & Standards, Page web: www.epa.gov/ttnuatw1/htthef/arsenic.html

Yamauchi, H., and Fowler, B.A., 1994, "Toxicity and Metabolism of Inorganics and Metlylated Arsenicals", in *Arsenic in the Environment*, Part II: Human Health and Ecosystem Effects, J.O. Nriagu (Editor), Wiley, New York.

1.4 Effects on Copper Properties

Braun, T.B., Rawling, J.R., and Richards, K.J., 1976, "Factors Affecting the Quality of Electrorefined Cathode Copper", in *International Symposium on Copper Extraction and Refining, Vol. I: Extractive Metallurgy of Copper, Pyrometallurgy and Electrolytic Refining,* J.C. Yannopoulos and J.C. Agarwal (Editors), Las Vegas, NV, pp. 511-524.

1.5 Solution Chemistry of Arsenic

Adam, K. Papassiopi, K., and Kontopoulos, A., 1994, "Stability of Arsenical Bacterial Oxidation Products", in *Hydrometallurgy'94,* Chapman and Hall – IMM, pp. 291-311.

Angeli, J., and Souchay, P., 1960, "On the Thioarsenates in Solution", *Compt. Rend.,* 250, pp. 713-715.

Barton, P.B., Jr., 1969, "Thermochemical Study of the System Fe-As-S", *Geochimica et Cosmochimica Acta,* 33, pp. 841-857.

Barton, P.B., Jr., and Skinner, B.J., 1979, "Sulfide Mineral Stabilities", in *Geochemistry of Hydrothermal Ore Deposits,* H. Barnes (Editor), Wiley, New York, pp. 278-403.

Beilina, A.Z., et al., 1979, "Synthesis and Study of Iron (III) Arsenate", *Zhur. Neorg. Khim.,* 24, pp. 2255-2258.

Belzine, N., and Tessier, A., 1990, "Interactions Between Arsenic and Iron Oxyhydroxides in Lacustrine Sediments, *Geochim. Cosmochim. Acta,* 59, pp. 103-109.

Carageorgos, T., 1995, "Stability of Arsenate Compounds From Oxidation of Gold Refractory Mineral", in *Latin American Perspectives: Exploration, Mining, and Processing,* O.A. Bascur (Editor), AIME, pp. 347-359.

Cartledge, F.K., 1993, "Solidification/Stabilization of Arsenic Compounds", in *Mercury and Arsenic Wastes: Removal, Recovery, Treatment, and Disposal,* Pollution Technology Review N° 214, US EPA (Editor), NJ, pp. 119-122.

Cassity, W.D., and Pesic, B., 1999, "Interactions of *Thiobacillus Ferrooxidans* with Arsenite, Arsenate and Arsenopyrite", in *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part A: Bioleaching, Microbiology, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, June 20-23, pp. 521-532.

Chukhlantsev, V.G., 1956, "The Solubility Product of Metal Arsenates", *Zhur. Neorg. Khim.,* 1, pp. 1975-1982.

Chukhlantsev, V.G., 1956, "The Solubility Product of Metal Arsenates", *Zhur. Analitichesikoi Khimii,* 11, pp. 529-535.

Chukhlantsev, V.G., 1956, "Solubility Products of a Series of Arsenates", *Zhur. Analitichesikoi Khimii,* 11, pp. 565-571.

Chukhlantsev, V.G., 1957, "The Solubility of Arsenious Acid Salts", *Zhur. Analitichesikoi Khimii,* 2, pp. 1190-1193.

Chung, Y., 1989, "Kinetic Study on Oxidation of Trivalent Arsenic to Pentavalent Arsenic with Various Types of Oxidant", *M. Sc. Thesis*, Montana Tech College Min. Sci. Tech., Butte, MT, USA.

Collins, M.J., Berezowsky, R.M., and Wier, D.R., 1988, "The Behaviour and Control of Arsenic in the Pressure Oxidation of Uranium and Gold Feedstocks", in *Arsenic Metallurgy Fundamentals and Applications,* Reddy, R.G., Hendrix, J.L., and Queneau, P.B. (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 115-134.

Dove, P.M., 1984, "The Solubility and Stability of Scorodite, $FeAsO_4 \cdot 2H_2O$", *M.S. Thesis,* Virginia Polytechnic Institute and State University, Blacksburg, VA.

Dove, P.M., and Rimstidt, J.D., 1985, "The Solubility and Stability of Scorodite, $FeAsO_4 \cdot 2H_2O$", *American Mineralogist,* 70, pp. 838-844.

Dutré, V., and Vandecasteele, C., 1995, "Solidification/Stabilisation of Arsenic-containing Waste: Leach Tests and Behaviour of Arsenic in the Leachate", *Waste Management,* 15:1, pp. 55-62.

Dutrizac, J.E., Jambor, J.L., and Chen, T.T., 1987, "The Behaviour of Arsenic during Jarosite Precipitation: Reaction at 150°C and the Mechanism of Arsenic Precipitation", *Canadian Metall. Quart.,* 26:2, pp. 103-115.

Dutrizac, J.E., and Jambor, J.L., 1988, "The Synthesis of Crystalline Scorodite, $FeAsO_4 \cdot 2H_2O$ ", *Hydrometallurgy,* 19, pp. 377-384.

D'Yvoire, F., and Ronis, M., 1968, "Preparation et Evolution Thermique de Scorodite Stoechiometrique, $FeAsO_4 \cdot 2H_2O$, et Non Stoechiometrique, $Fe_{1-x}H_{3x}AsO_4 \cdot 2H_2O$, *Acad. des Sciences,* Paris, Compters Rendus Hebdomadaires des Sceances, Serie C, 267, pp. 827-830.

Ehrlich, H.L., 1964, "Bacterial Oxidation of Arsenopyrite and Enargite", *Economic Geology,* 59, pp. 1306-1312.

Emmet, M.T., and Khoe, G., 1994, Environmental Stability of Arsenic Bearing Hydrous Iron Oxide Compounds", *EPD Congress 1994,* G.W. Warren (Editor), TMS, Warrendale, PA, pp. 153-166.

Grossin, C., 1993, "Etude de la Morphologie et de la Stabilité des Arseniates de Fer Synthetiques", *Ph.D. Thesis,* U.F.R. Faculté des Sciences, Université D'Orleans, France.

Guerin, H., 1938, "On the Alkaline Earth Arsenates: Study of the System As_2O_5-BaO-H_2O at 17°C", *Bull. Soc. Chim.,* France, 5:5, pp. 1472-1478.

Gulens, J., Champ, D.R., and Jackson, R.E., 1979, "Influence of Redox Environments on the Mobility of Arsenic in Ground Water", in *Chemical Modeling in Aqueous Systems,* E.A. Jenne (Editor), ACS Symposium Series, 93, Washington, DC, pp. 81-95.

Hartshorne, N.H., 1927, "The System Ferric Oxide-arsenic Acid-water at Low Concentrations of Arsenic Acid", *J. Chem. Soc.,* London, 2, pp. 1759-1768.

Hiskey, J.B., and Sánchez, V., 1988, "An electrochemical Study of the Surface Oxidation of Arsenopyrite in Alkaline Media", in *Arsenic Metallurgy Fundamentals and Applications,* Reddy, R.G., Hendrix, J.L., and Queneau, P.B. (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 59-75.

Itagaki, K., and Nishimura, T., 1986, "Thermodynamic Properties of Compounds and Aqueous Species of VA Elements", *Met. Review of MMIJ,* 3:2, pp. 29-48.

Iwai, M., Majina, H., and Awakura, Y., 1984, "Oxidation of As(III) with Oxygen in Alkaline Solutions in the Presence of Cu(II)", *J. Japan Inst. Metals,* 48, pp. 272-277.

Jain, A., Raven, K., and Loeppert, R.H., 1999, "Arsenite and Arsenate Adsorption on Ferrihydrite: Surface Charge Reduction and Net OH^- Release Stoichiometry", *Environ. Sci. Technol.,* 33, pp. 1179-1184.

Johnson, G.K., Papatheodorou, G.N., and Johnson, C.E., 1980, "The Enthalpies of Formation and High Temperature Thermodynamic Functions of As_4S_4 and As_2S_3", *J. Chem. Thermodynamics,* A-167, pp. 545-557.

Jones, C.A., Bozeman, W.P., and Neumanm, D.R., 1997, "Arsenic Transport in Contaminated Mine Tailings Following Liming", *J. Environ. Quart.,* 26:2, pp. 423-429
Jonna Lagadda, S.B., and Nenzou, G., 1997, "Studies on Arsenic Rich Mine Dumps", *J. Environ. Sci.,* VA32:2, pp. 455-564.

Kersten, M., 1992, "Geochemistry of Priority Pollutants in Anoxic Sludges: Cadmium. Arsenic, Methyl Mercury and Chlorinated Organics", in *Chemistry and Biology of solid Waste: Dredged Material and Mine Tailings,* Springer-Verlag, New York.

Khoe, G., 1992, "The Stability of Iron Arsenate Compounds", in *Innovations in Gold and Silver Recovery,* Randol, pp. 8678-8681.

Khoe, G., Carter, M., Emett, M., Vance, E.R., and Zaw, M., 1987, "The Stability and Immobilisation of Iron Arsenates Compounds", in *6th Australian IMM Extractive Metallurgy Conference,* Brisbane, pp. 281-286.

Khoe, G., and Robins, R.G., 1988, "The Complexation of Iron(III) with Sulphate, Phosphate, or Arsenate Iron in Sodium Nitrate Medium at 25°C", *J. Chem. Soc. Dalton Trans.,* pp. 2015-2021.

Know, O.J., and Robins, R.G., 1973, "Thermal Precipitation in Aqueous Solutions", in *International Symposium on Hydrometallurgy,* D.J. Evans and R.S. Shoemaker (Editors), AIME, Chicago, IL, pp. 1033-1080.

Krause, E., and Ettel, V.A., 1988, "Solubility and Stability of Scorodite, $FeAsO_4 \cdot 2H_2O$: New Data and Further Discussion", *American Mineralogist,* 73, pp. 850-854.

Mah, A.D., 1982, "Thermodynamic Data for Arsenic Sulfide Reactions", Bureau of Mines Report of Investigations, US Department Interior.

Makmetov, M.Zh., et al., 1974, "Synthesis of Iron Arsenates and Arsenites", *Deposit. Doc.,* VINITI, pp. 467-474.

Makmetov, M.Zh., et al., 1974, "Conditions for the Formation of Iron Arsenates and Their Thermal Stability", *Zhur. Prikl. Khim.,* 53:7, pp. 1625-1627.

Makmetov, M.Zh., et al., 1981, "Studies of Solubilities of Iron Arsenates", *Zhur. Prikl. Khim.,* 54:5, pp. 1009-1011.

Masscheleyn, P.H., Delaune, R.D., and Patrick, W.H., Jr., 1991, "Effect of Redox Potential and pH on Arsenic Speciation and Solubility in a Contaminated Soil", *Environ. Sci. Technol.*, 25:8, pp. 1414-1419.

Masuko, N., and Shibuta, D., 1976, "Limits of Arsenic Removal by Precipitation Methods", *J. Inst. Industrial Science*, University of Tokyo, 28, pp. 104-108.

Molnar, L., Vircikova, E., and Lech, P., 1994, "Experimental Study of As(III) Oxidation by Hydrogen Peroxide", *Hydrometallurgy*, 33, pp. 1-9.

Monhemius, A.J., 1977, "Precipitation Diagrams for Metal Hydroxides, Sulfides, Arsenates and Phosphates", *Trans. Inst. Min. Met. C*, 86, pp. 202-206.

Monhemius, A.J., 1996, "Hydrometallurgy – the Clean Solution for Metal Production? in clean Technologies for the Mining Industry", in *III International Conference on Clean Technology for the Mining Industry*, M. A. Sánchez, F. Vergara and S.H. Castro (Editors), Santiago, Chile, 15-17 May, pp. 113-124.

Monhemius, A.J., and Swash, 1996, "The Iron(III) – Arsenic(V) System and its Application to Arsenic Disposal", in *Iron Control Short Course, Second International Symposium on Iron Control*, CIM, Ottawa, Canada, October 19-23.

Nan, L., and Lawson, F., 1989, "Kinetics of Heterogenerous Reduction of Arsenic(V) to Arsenic(III) with Sulphur Dioxide", *Hydrometallurgy*, 22, pp. 339-351.

Nishimura, T., and Tozawa, K., 1978, "On The Solubility Product of Ferric, Calcium and Magnesium Arsenates", *Bulletin Research Inst. Min. Dress. Met.*, Tohoku University, 34, pp. 20-26 (in Japanese).

Nishimura, T., and Tozawa, K., 1986, "Behaviour of Antimony and Arsenic in Sulfuric Acid Solution", in *Metallurgical Review of MMIJ*, 3:2, pp. 131-145.

Nishimura, T., Palacios, J., and Tozawa, K., 1988, "Oxidative Ammonia Leaching of a Copper-Arsenic Deposit and the Oxidation of As(III)", *Bull. Res. Inst. Min. Dress. Metall.*, Tohoku University, Japan, 44:1, pp. 87-100 (in Japanese).

Nishimura, T., and Tozawa, K., 1988, "Kinetics of Oxidation of Arsenious Acid with Aqueous Ozone", *J. Min. Met. Inst. Japan*, 104, pp. 549-553.

Nishimura, T., and Robins, R.G., 1996, "Crystalline Phases in the system Fe(III)-As(V)-H_2O at 25°C", in *Iron Control and Disposal*, Proceedings of the Second International Symposium on Iron Control in Hydrometallurgy, J.E. Dutrizac and G.B. Harris (Editors), CIM, Ottawa, Canada, pp. 521-534.

Nishimura, T., Tozawa, K., and Robins, R.G., 1983, "The Calcium-Arsenic-Water System", in *Proceedings MMIJ/Australian IMM Joint Symposium*, session JD, paper 2, Sendai, Japan, October, pp. 105-120.

Nordstrom, D.K., 2000, "Thermodynamic Properties of Environmental Arsenic Species: Limitations and Needs", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 325-332.

Pakholkov, V.S., Dvinin, S.G., and Markov, V.F., 1980, "Sorption of As(III) and As(V) from Aqueous Solution by Hydrated Oxides and Inorganic Ion-Exchangers Based on Them", *Zh Prikl. Khim,* 53:2, pp. 280-285.

Papassiopi, N., Stefanakis, M., and Kontopoulos, A., 1994, "Crystalline Ferric Arsenates; Structure and Stability Studies", in *EMC '94 Metallurgy I,* GDMB Informationsgesellschaft mbH, Clauthal-Zellerfeld, pp. 203-212.

Pierce, M.L., 1981, "Chemical Modeling of Arsenic in Aqueous Systems", *Ph.D. Thesis,* Arizona State University, Phoenix, AZ, May 1981.

Pierce, M.L., and Moore, C.B., 1980, "Adsorption of Arsenite on Amorphous Iron Hydroxide from Dilute Aqueous Solution", *Environ. Sci. Technol.,* 14, pp. 214-216.

Pierce, M.L., and Moore, C.B., 1982, "Adsorption of Arsenite and Arsenate on Amorphous Iron Hydroxide", *Water Research,* 16, pp. 1247-1253.

Raade, G., Sasaki, K., Kristiansen, R., and Din, V.K., 1984, "Kaatialaite, a New Ferric Arsenate Mineral from Finland", *American Mineralogist,* 69, pp. 383-387.

Robins, R.G., 1983, "The Stabilities of Arsenic (V) and Arsenic (III) Compounds in Aqueous Metal Extraction Systems", in *Hydrometallurgy Research Development and Plant Practice,* K. Osseo-Asare and J.D. Miller (Editors), The Metallurgical Society, Warrendale, PA, pp. 291-310.

Robins, R.G., 1993, "Arsenic Chemistry in Relation to the Disposal and Stability of Metallurgical Extraction Wastes", in *Mercury and Arsenic Wastes: Removal, Recovery, Treatment, and Disposal,* Pollution Technology Review N° 214, US EPA (Editor), New Yersey, pp. 63-65.

Robins, R.G., Twidwell, L.G., and Dahnke, D.R., 1986, "Solubility Diagrams for Aqueous Metal Phosphate Systems", in *2nd International Symposium on Solubility,* Newark, NJ, pp. 1-22.

Robins, R.G., and Glastras, M.V., 1987, "The precipitation of Arsenic from Aqueous Solution in Relation to Disposal from Hydrometallurgical Processes", in *Research and Development in Extractive Metallurgy,* Aus. Inst. Min. Metall., Adelaide, pp. 223-229.

Robins, R.G., Dove, P.M., Rimstidt, J.D., Nordstrom, D.K., and Parks, G.A., 1987, "The Solubility and Stability of Scorodite, $FeAsO_4 \cdot 2H_2O$", *American Mineralogist,* 72, pp. 842-855.

Robles, A., Serna, A.E., and Sández, M., 1999, "Estudio Cinético de la Oxidación Catalítica del Arsénico por Medio del Uso de Cobre Metálico", in *IX Congreso Internacional de Metalurgia Extractiva*, L.A. Almazán Holguin, et al. (Editors), Universidad de Sonora – Hermosillo, pp. 155-164.

Seidell, A., and Linke, W.F., *Solubilities: Inorganic and Metal Organic Compounds*, Van Nostrand, Princeton, NJ, 1958.

Stronach, S.A., Walker, N.L., Macphee, D.E., and Glasser, F.P., 1997, "Reactions Between Cement and As (III) Oxide: the System CaO-SiO_2-As_2O_3-H_2O at 25°C", *Waste Management*, 17:1, pp. 9-13.

Swash, P.M., 1996, "The Hydrothermal Precipitation of Arsenical Solids in the Ca-Fe-AsO_4-SO_4 System at Elevated Temperatures", *Ph.D. Thesis*, Imperial College, University of London, UK.

Swash, P.M. and Monhemius, A.J., 1994, "The Hydrothermal Precipitation from Aqueous Solutions Containing Iron(III), Arsenate and Sulfate", in *Hydrometallurgy 94*, Proceedings of Conference in Cambridge, UK, IMM, Chapman and Hall, pp. 177-190.

Swash, P.M. and Monhemius, A.J., 1995, "Hydrothermal Precipitation, Characterisation and Solubility Testing of Solids in the Ca-Fe-AsO_4 System", in *Sudbury '95, Mining and the Environment*, Volume I, Sudbury, Ontario, pp. 17-28.

Swash, P.M., Monhemius, A.J., and Schaekers, J.M., 2000, "Solubilities of Process Residues from Biological Oxidation Pretreatments of Refractory Gold Ores", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi*, C. Young (Editor), SME, Littleton, CO, pp. 115-124.

Swash, P.M. and Monhemius, A.J., 1996, "Calcium Arsenate Compounds and their Significance in Metallurgical Processing", in *Metals and the Environment II*, IMM, Prague, Czech Republic, pp. 353-361.

Takahashi, T., and Sasaki, K., 1950, "The Equilibrium for the System Fe_2O_3-As_2O_5-H_2O", *J. Chem. Soc.*, Japan, Industrial Chemistry Section, 53, pp. 383-384.

Thanabalasingam, P., and Pickering, W.F., 1986, "Effect of pH on Interaction between As(III) or As(V) and Manganese (IV) oxide", *Water, Air, Soil Pollution*, 29, pp. 205-216.

Tozawa, K., and Nishimura, T., 1973, "Oxidation of Arsenic (III) in Aqueous Solution", *J. Min. Met. Inst. Japan*, 92, pp. 809-814.

Tozawa, K., and Nishimura, T., 1976, "Oxidation of As(III) in Aqueous Solution", *J. Min. Met. Inst. Japan*, 92, pp. 809-814.

Tozawa, K., and Nishimura, T., 1978, "The Arsenic-Sulfur-Water System", *Bull. Res. Ins. Min. Dress. Met.*, Tohoku University, 34:1, pp. 74-79.

Tozawa, K., and Nishimura, T., 1984, "Oxidation of As (III) to As (V) in Aqueous Solutions", *Met. Review MMIJ*, 1, pp. 76-87.

Ugarte, F.J.G., and Monhemius, A.J., 1992, "Characterisation of high-Temperature Arsenic-containing Residues from Hydrometallurgical Processes", *Hydrometallurgy*, 30, pp. 69-86.

Vink, B.W., 1996, "Stability Relations of antimony and Arsenic Compounds in the Light of Revised and Extended Eh-pH Diagrams", *Chemical Geology*, 130, pp. 21-30.

Vircikova, E., Molnar, L., Lech, P., and Reitznerova, E., 1995, "Solubilities of Amorphous Fe-As Precipitates", *Hydrometallurgy*, 38, pp. 111-123.

Yoshida, I., Kobayashi, H., and Ueno, K., 1976, "Selective Adsorption on Arsenic Ions Impregnated with Ferric Hydroxide", *Analytical Letters*, 9:12, pp. 1125-1133.

Young, C.A., Robins, R.G., 2000, "The Solubility of As_2S_3 in Relation to the Precipitation of Arsenic from Process Solutions", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi*, C. Young (Editor), SME, Littleton, CO, pp. 381-392.

Zhang, W., Singh, P., and Muir, D.M., 2000, "Kinetics of Oxidation of As (III) with SO_2/O_2 and UV Light", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi*, C. Young (Editor), SME, Littleton, CO, pp. 333-344.

Zinck, J.M., 2000, "The Abundance, Behaviour, and Stability of As, Cd, Pb, and Se in Lime Treatment Sludges", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi*, C. Young (Editor), SME, Littleton, CO, pp. 213-224.

1.6 Analytical Techniques for the Measurement of Arsenic

Crock, J.G., and Lamothe, P.J., 2000, "A Short Review of the Current Environmental Analytical Chemistry of As, Sb, Se, Te, and Bi", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi*, C. Young (Editor), SME, Littleton, CO, pp. 75-94.

Francesconi, K.A., Edmonds, S., and Morita, M., 1994, "Determination of Arsenic and Arsenic Species in Marine Environmental Samples", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 189-220.

Haywood, M.G., and Riley, J.P., 1976, "The Spectrophotometric Determination of Arsenic in Sea Water, Potable Water and Effluents, *Analytica Chimica Acta*, 85, pp. 219-230.

Kingsley, G.R., and Shaffert, R.R., 1951, "Microdetermination of Arsenic and its Application to Biological Material", *Analy. Chem.*, 23, pp. 914-919.

US EPA, 2000, "Method 108: Determination of Particulate and Gaseous Arsenic Emissions", Office and Air Quality, Planning and Standards.
Page web: http://www.epa.gov/ttnemc01/promgate/m-108.pdf

US EPA, 2000, "Method 108a: Determination of Arsenic in Ore Samples from Nonferrous Smelters", Office and Air Quality, Planning and Standards.
Page web: http://www.epa.gov/ttnemc01/promgate/m-108a.pdf

US EPA, 2000, "Method 108b: Determination of Particulate and Gaseous Arsenic Emissions", Office and Air Quality, Planning and Standards.
Page web: http://www.epa.gov/ttnemc01/promgate/m-108b.pdf

1.7 Production, Consumption and Uses of Arsenic

Baldwin, W.J., 1988, "The Use of Arsenic as a Wood Preservative-An Update", in *Arsenic Metallurgy Fundamentals and Applications*, Reddy, R.G., Hendrix, J.L., and Queneau, P.B. (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 507-514.

Broome, A.D.J., Fowlie, D.A., Preston, A.F., 1988, "The Production and Use of Arsenicals in Wood Preservation", in *Arsenic Metallurgy Fundamentals and Applications*, Reddy, R.G., Hendrix, J.L., and Queneau, P.B. (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 491-506.

Edelstein, 1983, D.L., "Arsenic", in *Mineral Facts and Problems*, US Bureau of Mines, Washington, DC, pp. 43-52.

Edelstein, D.L., 1997, "Arsenic: Domestic Production and Use in the US",
Web site: http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/160397.pdf

US Geological Survey, "Arsenic: Statistics and Information".
Web site: http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/

1.8 Ambient Standards and Guidelines

Galal-Gorchev, H., 1997, "World Health Organization Guideline Value for Arsenic in Drinking Water", in *Consultation on Arsenic in Drinking Water and Resulting Arsenic Toxicity in India and Bangladesh*, WHO, New Delhi, India.

Ministère de l'environnement du Québec, 1997, *Règlement sur la qualité de l'atmosphère*, Sainte-Foy, Qc, Canada.

Traulsen, H.R., Taylor, J.C., and George, D.B., 1982, "Copper Smelting - An Overview", *JOM*, 34:8, pp. 35-40.

US EPA, 1980, “Ambient Water Quality Criteria for Arsenic”, Report: EPA-440/5-80-021.

US EPA, 1995, “Profile of the Nonferrous Metals Industry”, Report: EPA-310/R-95-010, National Environmental Publications Information.

US EPA, 1997, “National air Polluant Emission Trends Update, 1900-1996”, Report: EPA 454/R-97-011, Office of Air Quality Planning and Standards.
Page web: http://www.epa.gov/ttn/chief/trends96/report97.html

US EPA, 1997, “Arsenic in Drinking Water: Regulatory History”, Office of Ground Water and Drinking Water. Page web: www.epa.gov/OGWDW/ars/ars1.html

US EPA, 1998, “National Air Quality and Emissions Trends Report, 1997”, Report EPA-454/R-98-016, Office of Air Quality Planning and Standards.
Page web: http://www.epa.gov/oar/aqtrnd97/toc.html

US EPA, 1998, “National Emission Standards for Hazardous Air Polluants for Source Categories: National Emission Standards for Primary Copper Smelters; Proposed Rule”, *Federal Register*, Part II: Environmental Protection Agency.
Page web: www.epa.gov/ttn/oarpg/t3/fr_notices/prcopper.pdf

US EPA, 1998, “National air Polluant Emission Trends Update, 1970-1997”, Report: EPA-454/E-98-007, Office of Air Quality Planning and Standards.
Page web: http://www.epa.gov/ttn/chief/trends97/browse.html

US EPA, 2000, “National Air Quality and Emissions Trends Report, 1998”, Report: EPA-454/R-00-003, Office of Air Quality Planning and Standards.
Page web: http://www.epa.gov/oar/aqtrnd98/toc.html

WHO, 1987, *Air Quality Guidelines for Europe*, Copenhagen: World Health Organization.

1.9 Arsenic Removal from Drinking Water

Bajpai, S., and Chaudhuri, M., 1999, “Removal of Arsenic From Ground Water by Manganese Dioxide-Coated Sand”, *Journal of Enviromental Engineering*, 125:8, pp. 782-784.

Bellack, E., 1971, “Arsenic Removal from Potable Water”, *J. Amer. Water Works Association*, 63, pp. 454-458.

Bhattacharya, P., Chatterjee, D., Jacks, G., 1997, “Options for Safe Drinking Water Supply”, *Int. J. Water Resources Management*, 13:1, pp. 79-92.

Driehaus, W., Jekel, M., and Hildebrandt, U., 1998, "Granular Ferric Hydroxide - A New Adsorbent for the Removal of Arsenic from Natural Water", *J. Water Sci. Research Tech. - Aqua,* 47:1, pp. 30-35, Blackwell Science, UK.

Driehaus, W., Seith, R., and Jekel, M., 1995, "Oxidation of Arsenate (III) with Manganese Oxides in Water Treatment", *Water Research*, 29:1, pp. 297-305, Blackwell Science, UK.

Dutta, A., and Chaudhuri, M., 1991, "Removal of Arsenic From Groundwater by Lime Softening with Powdered Coal Additive", *Aqua*, 41:1, pp. 25-29.

Edwards, M., 1994, "Chemistry of Arsenic Removal During Coagulation and Fe-Mn Oxidation", *J. Amer. Water Works Association*, 86:9, pp. 64-78.

Fox, K.R., and Sorg, T.J., 1987, "Controlling Arsenic, Fluoride and Uranium by Point-of-use Treatment", *J. of Amer. Water Works Association*, 79, pp. 81-84.

Gullege, J.H., and O'Connor, J.T., 1973, "Removal of Arsenic (V) from Water by Adsorption on Aluminum and Ferric Hydroxides", *J. AWWA,* 65:8, pp. 548:552.

Hathaway, S.W., and Rubel, F., 1987, "Removing Arsenic from Drinking Water", *J. Amer. Water Works Association,* 79, pp. 61-65.

Hering, J.G., Chen, P.Y., Wilkie, J.A., Elimelech, M., and Liang, S., 1996, "Arsenic Removal by Ferric Chloride", *J. Amer. Water Works Association*, 88:4, pp. 155-167.

Hering, J.G., Chen, P.Y., Wilkie, J.A., and Elimelech, M., 1997, "Arsenic Removal From Drinking Water During Coagulation", *J. Environ. Eng.*, 123:8, pp. 800-807.

Hounslow, A.W., 1980, "Ground-water Geochemistry: Arsenic in Landfills", *Ground Water*, 18:4, pp. 331-333.

Khoe, G.H., Emett, M.T., Zaw, M., and Prasad, P., 2000, "Removal of Arsenic Using Advanced Oxidation Processes", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 31-38.

Jekel, M.R., 1994, "Removal of Arsenic in Drinking Water Treatment", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 119-132.

Lehimas, G.F., Chapman, J.I., and Bourgine, F.P., 1999, "Use of Biological Processes for Arsenic Removal: A cost effective alternative to chemical treatment for As(III) in groundwater". Available on internet: http://www.saur.co.uk/poster.html

Mukherji, S.N., "Arsenic Management in Drinking Water", 1997, in *Consultation on Arsenic in Drinking Water and Resulting Arsenic Toxicity in India and Bangladesh,* WHO, New Delhi, India.

Nikolaidis, N.P., Lackovic, J., and Dobbs, G., 1999, "Arsenic Remediation Technology – AsRT". Page web: http://www.eng2.uconn.edu/~nikos/asrt-brochure.html

Prasad, G., 1994, "Removal of Arsenic(V) from Aqueous Systems by Adsorption Onto some Geological Materials", in *Arsenic in the Environment, Part I: Cycling and Characterization*, J.O. Nriagu (Editor), Wiley, New York, pp. 133-154.

Rubel, F., and Hathaway, S.W., 1987, "Pilot Study for the Removal of Arsenic from Drinking Water at the Fallon, Nevada, Naval Air Station", *J. Amer. Water Works Association,* 79, pp. 61-65.

Shen, Y.S., 1973, "Study of Arsenic Removal From Drinking Water", *J. Amer. Water Works Association,* 65, pp. 543-548.

Vaishya, R.C., and Agarwal, I.C., 1993, "Removal of Arsenic (III) From Contaminated Ground Waters by Ganga Sand", *J. Indian Water Works Association,* 25:3, pp. 249-253.

US EPA, 1998, "Research Plan for Arsenic in Drinking Water", Report: *EPA/600/R-98/042,* Office of Research and Development, Washington, Dc.
Page web: http://www.epa.gov/cgi-bin/claritgw?op-Display&document=clserv:epa-cin9:807;&rank=10&template=epa

2. ARSENIC DISTRIBUTION IN COPPER SMELTERS

Björkman, B., Eriksson, J., Nedar, L., and Samuelsson, C., 1996, "Waste Reduction Through Process Optimization and Development", *JOM,* 48:3, pp. 45-49.

Brittain, R.D., Lau, K.H., and Lamoreaux, R.H., 1983, "Studies of the Volatilization Chemistry of Arsenic in Sulfide Smelting Phases", in *Sulfide Smelting, Vol. II.,* pp. 197-215

Carrera, E., 1996, "Arsenic Control in the Sulfuric Acid Plant by the Purification System of Caraíba Metais", in *EPD Congress 1996,* G.W. Warren (Editor) TMS, Warrendale, PA, pp. 923-935.

Cordova, P. and Szczgiel, Z., 1999, "Problemas con el Arsénico en la Pirometalurgia no Ferrosa del Cobre y del Zinc", in *IX Congreso Internacional de Metalurgia Extractiva,* L.A. Almazán Holguin et al. (Editors), Universidad de Sonora – Hermosillo, pp. 183-193.

Cram, J.N., 1972, "Arsenic in Pyrometallurgical Operations", in *Proceedings of the Fourth Annual Meeting of the CMP,* CIM, Montreal, pp. 205-217.

Czernecki, J., Smieszek, Z., Gizicki, S., Dobrzanski, J., and Warmuz, M., 1998, "Problems with Elimination of the Main Impurities in the KGHM Polska Miedz S.A. Copper Concentrates from the Copper Production Cycle (Shaft Furnace Process, Direct Blister Smelting in a Flash Furnace", in *Sulfide Smelting '98: Current and Future Practices*, TMS Annual Meeting, San Antonio, TX, pp. 315-344.

Dalewski, F., and Piret, N.L., 1995, "Environmental Implications of the Process Selection for Arsenic Removal from SO_2-Bearing Gases and Downstream Treatment", in *Copper 95-Cobre 95 International Conference*, Volume II: Mineral Processing and Environment, A. Casali, G.S. Dobby, M. Molina and W.J. Thoburn (Editors), Metallurgical Society of CIM, Santiago, Chile, pp. 399-420.

Daum, K.H., and Sneyd, R.J., 1992, "Gas Purification for Metallurgical Sulphuric Acid Plants", in *Proceedings of the International Symposium on Non-Ferrous Pyrometallurgy: Traces Metals, Furnace Practices and Energy Efficiency*, R. Bergman (Editor), CIM, Edmonton, Canada, pp. 85-106.

Evrand, L., Boydens, E., Brouwer, S., and Van Camp, M., 2000, "Behavior of As and Sb in Hoboken Lead Sinter", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 251-258.

Itagaki, K., 1986, "Thermodynamic Evaluation of Distribution, Behaviour of VA Element and Effect on the Use of Oxygen in Copper Smelting", *Metallurgical Review MMIJ,* Vol. 3, pp. 87-100.

Itagaki, K., and Yazawa, A., 1983, "Thermodynamic Evaluation of Distribution of Arsenic, Antimony, and Bismuth in Copper Smelting", in *Sulfide Smelting,* Vol. 1, TMS-AIME, pp. 119-142.

Itagaki, K., and Yazawa, A., 1985, "Thermodynamic Properties of Arsenic and Antimony in Copper Smelter Systems", in *Symposium on Complex Sulfide,* TMS-AIME, San Diego, CA, pp. 705-722.

Kim, H.G., and Sohn, H.Y., 1996, "Thermodynamic Modelling of Minor-element Behaviour in In-bath Copper Smelting and Converting with Calcium Ferrite Slag", *Trans. Instn. Min. Metall. (Sect. C),* 105, pp. C151-C163.

Larouche, P., 2000, "Control of Minor Elements in Copper Smelting and Electrorefining", *M. Eng. Thesis*, Dep. of Mining and Metallurgical Engineering, McGill University, Montreal, Canada.

MacCaig, R.B., and Cianciarelli, D.J., 1984, *Report on the Emission Testing of Arsenic and Sulphur at Giant Yellowknife mines Ltd., Yellowknife,* Environment Canada, Environmental Protection Service, 22p.

Mackey, P.J., McKerrow, G.C., and Tarassoff, P., 1975, "Minor Elements in the Noranda Process", in *104th Annual AIME Meeting,* New York, NY.

Maeda, Y., Inoue, H., Hoshikawa, Y., and Shirasawa, T., 1998, "Current Operation of Kosaka Smelter", in *Sulfide Smelting '98: Current and Future Practices*, TMS Annual Meeting, San Antonio, TX, pp. 305-314.

Mäkinen, J.K., and Jåfs, G.A., 1982, "Production of Matte, White Metal, and Blister Copper by Flash Furnace", *JOM*, 34:6, pp. 54-58.

Nagamori, M., and Mackey, P.J., 1978, "Thermodynamics of Copper Matte Converting: Part II: Distribution of Au, Ag, Pb, Zn, Ni, Se, Te, Bi, Sb, and As Between Copper, Matte and Slag in the Noranda Process", *Met. Trans. B*, AIME, 9B, pp. 567-579.

Nagamori, M., and Chaubal, P.C., 1982, "Thermodynamics of Copper Matte Converting: Part III: Steady-State Volatilization of Au, Ag, Pb, Zn, Ni, Se, Te, Bi, Sb, and As from Slag, Matte, and Metallic Copper", *Met. Trans. B*, AIME, 13B, pp. 319-329.

Piret, N.L., 1999, "The Removal and Safe Disposal of Arsenic in Copper Processing", *JOM*, 51:9, pp. 16-17.

Schlicher, R.J., and Ghosh, M.M., 1985, "Removal of Arsenic from Water by Physical-Chemical Processes", in *A.I. Ch. E. Symposium Series*, 82:243, pp. 152-164

Skeaff, J.M., and Dubreuil, A.A., 1998, "Calculated Emission Factors of Trace Metals for Canadian Non-ferrous Smelters", in *Proceedings of Metals and the Environment: An International Symposium*, J. Skeaff (Editor), 100th CIM Annual General Meeting, pp. 105-115.

Smith, T.J.A. and Newman, C.J. (Editors), 1992, "Smelter Process Gas Handling and Treatment", *Proceeding of an International Symposium*, Pyrometallurgical Committe, Annual Meeting of the Minerals, TMS, San Diego, CA.

Steinhauser, J., Vartiainen, A., and Wuth, W., 1984, "Volatilization and Distribution of Impurities in Modern Pyrometallurgical Copper Processing from Complex Concentrates", *JOM*, 36:1, pp. 54-61.

Valenzuela, A., Fytas, K., and Sánchez, M., 2000, "Arsenic Management in Pyrometallurgical Processes, Part I: Distribution in Smelting/Converting", in *V International Conference on Clean Technology for the Mining Industry*, Vol. II: Environmental Improvements in Mineral Processing and Extractive Metallurgy, M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile.

Weeks, T., and Wan, R.Y., 2000, "Behavoir of Arsenic in Refractory Gold Ore Processing – A Case Study of PT Newmont Minahasa Raya", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi*, C. Young (Editor), SME, Littleton, CO, pp. 125-134.

Yazawa, A., and Azakami, T., 1969, "Thermodynamics of Removing Impurities During Copper Smelting", *Can. Met. Quart.*, 8:3, pp. 257-261.

Zeping, Y., 1998, "Impurity Distribution and Removal Practice in the Copper Smelting Process at Guixi Smelter", in *Sulfide Smelting '98: Current and Future Practices*, TMS Annual Meeting, San Antonio, TX, pp. 345-352.

Zhao, B., and Themelis, N., 1996, "Kinetics of As and Sb Removal From Molten Copper by Na_2CO_3 Fluxing", in *EPD Congress 1996*, G.W. Warren (Editor) TMS, Warrendale, PA, pp. 515-525.

3. ENVIRONMENT MANAGEMENT IN THE CHILEAN COPPER INDUSTRY

Arteaga, J., and Duran, H., 1998, "Contaminación Atmosférica en Chile: Antecedentes y Políticas para su Control". Article on line: http://lauca.usach.cl/ima/cap.htm

Campos, R., Miranda, S., and Smith, T.J.A., 1998, "Refimet Smelter Operation and Development", in *Sulfide Smelting '98: Current and Future Practices*, TMS Annual Meeting, San Antonio, TX, pp. 519-534.

Castro, S.H., Sánchez, M.A., Vergara, F. and Oyaneder, E., 1998, "Water and Slurry Wastes Assessment in the Chilean Copper Industry", *IV International Conference on Clean Technology for the Mining Industry*. M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 1005-1016.

Castro, S.H., Sánchez, M.A., Vergara, F., 1999, "Environmental Problems and Effluent Treatment in the Chilean Copper Industry", in *Copper 99-Cobre 99*, Volume II: Mineral Processing/Environment, Health and Safety, B.A. Hancock and M.R.L. Pon (Editors), TMS, AZ, pp. 297-305.

Environment Canada, 1996, "Environmental Management in Chile – Report, chapter 4". Page web: http://www.naaec.gc.ca/english/canchile/report/chilerepch4a_e.htm

Lagos, G., Lehuedé, J.M., and Andia, M., 2000, "Analysis of the Decontamination Plans of the Smelters of: Chuquicamata, Hernán Videla Lira (Paipote), and Ventanas", in *V International Conference on Clean Technologies for the Mining Industry,* Vol. I: Waste Treatment and Environmental Impact in the Mining Industry, M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile.

Mondschein, S., and Massai, R.,1998, "Descontaminación de las Fundiciones Estatales de Cobre", *Revista Minería Chilena,* 203, pp. 139-145.

O'Ryan R., and Díaz, M., 1998, "Risk-cost Analysis of Environmental Regulations for Arsenic in Chile", in *Environmental Issues and Waste Management in Energy and Mineral Production*, Paşamehmetoğlu and Özgenoğlu (Editors), Balkema, Rotterdam, pp. 111-116.

Revista Minería Chilena, "Medioambiente y Minería: Visión de CONAMA", N° 204, June 1998, pp. 71-75.

Romo-Kröger, C.M., Morales, J.R., Dinator, M.I., and Llona, F., 1994, "Heavy Metals in the Atmosphere Coming From a Copper Smelter in Chile", *Atmospheric Environment,* 28:4, pp. 705-711.

Sánchez, G., and Díaz, H., 1994, "Descontaminación Ambiental Area Fundición de Caletones: Una Tarea en Marcha", in *Proyecciones de la Minería Chilena a Nivel Internacional",* Convención Anual Instituto de Ingenieros de Minas de Chile, Chile.

Siegel, P.D., and de Siegel, E.A., 1992, "Chuquicamata's smelter arsenic pollution", in *Environmental Issues and Waste Management in Energy and Minerals Production,* R.K. Singhal, et al., (Editors), Balkema, Rotterdam, pp. 1129-1133.

Smith, T.J.A., Morgan, B.M., and Tidy, P.R., 1998, "Design and Operation of a Novel Gas Cooler for Refimet Copper Smelter, La Negra, Chile", in *Sulfide Smelting '98: Current and Future Practices*, TMS Annual Meeting, San Antonio, TX, pp. 433-442.

4. ARSENIC RECOVERY WORLDWIDE

4.1 From Copper Concentrates

Edwards, C.R., 1985, "Engineering The Equity Concentrate Leach Process", in *Complex Sulfides,* TMS, Warrendale, Pa, pp. 197-219.

4.2 From Gold Concentrates

Ramadorai, G., and Mishra, R.K., 1988, "Roasting of Arsenical Gold and Silver Bearing Minerals", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 161-171.

4.3 From Arsenic-containing Copper Smelter Dusts

Arsenault, R.D., 1993, "Recovery of Arsenic as a Raw Material for Reuse (Case Studies-Mining Wastes, Flue Dusts)", in *Mercury and Arsenic Wastes: Removal, Recovery, Treatment, and Disposal,* Pollution Technology Review N° 214, US EPA (Editor), NJ, pp. 72-78.

Bartlett, R.W., 1988, "Separation of As and Ga from Mixed GaAs Electronic Scrap", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 385-400.

Drinkard, Jr., W.F., 1992, "The Philosopher's Stone: The Transformation of Arsenic From Hazardous Waste to Commercial Products", in *Proceedings of the International Symposium on Non-Ferrous Pyrometallurgy: Traces Metals, Furnace Practices and Energy Efficiency*, R. Bergman (Editor), CIM, Edmonton, Canada, pp. 209-219.

Ishiguro, S., 1989, "Purification and Properties of High-purity Metallic Arsenic", in *Today's Technology for the Mining and Metallurgical Industries,* MMIJ/IMM Joint Symposium, Kyoto, Japan, pp. 539-547.

Kohno, H., Sugawara, Y., and Hashimoto, M., 1983, "Operation of Arsenic Trioxide Manufacturing Plant at Onahama Smelting & Refining Co. Ltd., in *112th Annual Meeting,* TMS-AIME.

Madsen, B.W., Dolezal, H., and Bloom, P.A., 1981, "Processing Arsenical Flue Dust with Sulfur Dioxide and Sulfuric Acid to Produce Arsenic Trioxide", in *110th AIME Annual Conference,* Chicago, IL, A81-63.

Neira, M.P., 1990, "Treatment of Copper Smelter Flue Dust for the Recovery of Elemental Arsenic", *M. Sc. Thesis,* Montana Tech College Min. Sci. Tech., Butte, MT, 113 p.

Palmer, B.R., Nami, F., and Fuerstenau, M.C., 1976, "Reduction of Arsenic Acid with Aqueous Sulfur Dioxide", *Met. Trans. B,* 7, pp. 385-390.

Polymbetova, K., Klimenko, V.L., and Auezov, Z., 1963, "Recovery of Arsenic from Converter Dust in the form of Commercial Calcium Arsenite", *Tsvet. Metall.,* 33:11, pp. 35-38.

Toyabe, K., and Nakajima, S., 1989, "High-purity Arsenic Metal Production and Its Application", in *Today's Technology for the Mining and Metallurgical Industries,* MMIJ/IMM Joint Symposium, Kyoto, Japan, pp. 531-537.

Tozawa, K., Umetsu, Y., and Nishimura, T., 1979, "A Hydrometallurgical Treatment of Arsenic-bearing Intermediate Products in smelters: Recovery of Valuable Metals and Arsenic Trioxide", *Bull. Res. Inst. Min. Dress. Metall.,* Tohoku University, 35, pp. 127-135.

Wolfe, J.R., 1983, "The Hydrometallurgical Recovery of Arsenic from Smelter flue Dust", in *Arsenic,* W.H. Lederer and R.J. Fensterheim (Editors), Van Nostrand Reinhold, New York, NY, pp. 10-15.

5. ARSENIC REMOVAL AND DISPOSAL FROM METALLURGICAL PROCESS

5.1 From Copper Concentrates

Achimovičová, M., Baláž, P., and Sánchez, M., 1998, "Alkaline Leaching of Arsenic and Antimony from Enargite ", *Acta Metallurgica Slovaca,* 4, Special Issue 1, pp. 33-37.

Baláž, P., 2000, "Antimony and Arsenic Extraction from Sulfides Pretreated by Mechanochemical Processing", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 285-292.

Charlton, T.L., and Redden, R.F., 1981, "Process for Extracting Arsenic from Oxidic Materials", *Canadian Patent: 1107514.*

Dayton, S., 1982, "Equity Silver on Line with Leach Plant", *E&MJ,* 183:1, pp. 78-83.

Kusik, C.L., Nadkarni, R.M., 1988, "Pyrometallurgical Removal of Arsenic from Copper Concentrates", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 337-349.

Long, H., and Dixon, D.G., 1999, "The Behavior of Orpiment During Pressure Oxidation: Part I, Chemistry", in *EPD Congress 1999,* B. Mishra (Editor), TMS, San Diego, CA, pp. 547-565.

Osmanso, R.D., 1977, "Investigations Concerning the Separation of Arsenic and Zinc Minerals From the Clyde E. Weed Final Copper Concentrates", *M. Sc. Thesis,* Montana Tech College Min. Sci. Tech., Butte, MT.

Padilla, R., Fan, Y., and Wilkomirsky, 1999, "Thermal Decomposition of Enargite", in *EPD Congress 1999,* B. Mishra (Editor), TMS, San Diego, CA, pp. 341-351.

Terry, D.S., and M.A., Sánchez, 1995, "Environmentally Friendly Processing of Copper Mineral Bearing Arsenic and/or Sulphur by Pyrometallurgical Route", in *Copper 95-Cobre 95 International Conference,* Volume II: Mineral Processing and Environment, A. Casali, G.S. Dobby, M. Molina and W.J. Thoburn (Editors), Metallurgical Society of CIM, Santiago, Chile, pp. 337-345.

Wiertz, J.V., Lunar, R., Maturana, H., and Escobar, B., 1999, "Bioleaching od Copper and Cobalt Arsenic-bearing Ores: A Chemical and Mineralogy Study", in *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part A: Bioleaching, Microbiology, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, pp. 397-404.

5.2 From Gold Concentrates

Abbruzzese, C., Ubaldini, S., and Veglio, F., 1998, "Behaviour of Pyrrhotite, Arsenopyrite and Stibnite to Biooxidation", *Acta Metallurgica Slovaca,* 4, Special Issue 1, pp. 19-24.

Acevedo, F., Canales, C., and Gentina, J.C., 1999, "Biooxidation of an Enargite-pyrite Gold Concentrate in Aerated Columns", in *Biohydrometallurgy and the* Environment *Toward the Mining of the 21st Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part A: Bioleaching, Microbiology, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, pp. 301-307.

Adam, K., Battaglia, F., Hau, J.M., Morin, D., Papassiopi, N., Tidy, N.E., and Pooley, F., 1997, "Bioleaching of Refractory Gold Arsenopyritic Concentrate From Batch Testwork to Cost Estimate", in *Proceedings XX International Mineral Processing Congress,* Volume 4: Solid-liquid Separation, Hydro- and Biohydrometallurgy, H. Hoberg, and H. von Blottnitz (Editors), Aachen, Germany, pp. 525-535.

Andrews, L., and Merkle, R.K.W., 1999, "Mineralogical Factors Affecting Arsenic Oxidation Rate During Acid Ferric Sulphate and Bacterial Leaching of Refractory Gold Ores", in *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part A: Bioleaching, Microbiology, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, pp. 109-117.

Beattie, M.J.V., and Ismay, A., 1990, "Applying the Redox Process to Arsenical Concentrates", *JOM,* 42:1, pp. 31-35.

Burcle, J., Marchant, G., and Meck, R., 1981, "Arsenic Emissions and Control in Gold Roasting Operations", *Environ. International,* 6, pp. 443-451.

Claassen, R., Logan, C.T., and Snyman. C.P., 1993, "Bio-oxidation of Refractory Gold-bearing Arsenopyrite Ores", in *Biohydrometallurgical Technologies,* Proceedings of an International Biohydrometallurgy Symposium, Volume I: Bioleaching Processes, A.E. Torma, J.E. Wey and V.I. Lakshmanan (Editors), Jackson hole, WY, August 22-25, pp. 479-488.

Diaz, M.A., and Gochin, R.J., 1994, "Flotation of Pyrite and Arsenopyrite at alkaline pH", *Trans. Instn. Min. Metall. (Sect. C),* 104, pp. C45-C49.

Dreisinger, D.B., and Saito, B.R., 1999, "The Total Pressure Oxidation of El Indio Ore and Concentrate", in *Copper 99-Cobre 99,* Volume IV: Hydrometallurgy of Copper, S.K. Young, D.B. Dreisinger, R.P. Hackl, and D.G. Dixon (Editors), TMS, Phoenix, AZ, pp. 181-195.

Hopkin, W., 1993, "Arsenical Residue Disposal in Refractory Gold Treatment", in *Randol Gold Forum Cairns '93,* Australia, pp. 191-195.

Koslides, T., and Ciminelli, V.S.T., 1992, "Pressure Oxidation of Arsenopyrite and Pyrite in Alkaline Solutions", *Hydrometallurgy,* 30, pp. 87-106.

Laguiton, D., 1976, "Arsenic Removal from Gold-mine Waste Waters: Basic Chemistry of the Lime Addition Method", *CIM Bulletin,* 69, pp. 105-109.

Lawrence, R.W., and Marchant, P.B., 1988, "Biochemical Pretreatment in Arsenical Gold Ore Processing", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 199-211.

Loayza, C., Ly, M.E., Yupanqui, R., and Román, G. , 1999, "Laboratory Biooxidation Tests of Arsenopyrite Concentrate for the Tamboraque Industrial Plant", in *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part A: Bioleaching, Microbiology, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, pp. 405-410.

Malatt, K.A., 1999, "Bacterial Oxidation of Pure Arsenopyrite by a Mixed Culture", in *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part A: Bioleaching, Microbiology, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, pp. 411-421.

Mortin, D., and Ollivier, P., 1989, "Pilot Practice of Continuous Bioleaching of a Gold Refractory Sulfide Concentrate with a High As Content", in *Biohydrometallurgy 1989,* International Symposium Proceeding, J. Hole (Editor), WY, pp. 563-576.

Nicol, M.J., and Guresin, N., 2000, "A Novel Approach to the Oxidation of Arsenical Refractory Gold Concentrates", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 157-170.

Nyashanu, R.M., Monhemius, A.J., and Buchanan, D.L., 1999, "The Effect of Ore Mineralogy on the Speciation of Arsenic in Bacterial Oxidation of Refractory Arsenical Gold Ores", in *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part A: Bioleaching, Microbiology, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, pp. 431-441.

Papangelakis, V.G., and Demopoulos, G.P., 1990, "Acid Pressure Oxidation of Arsenopyrite: Part I: Reaction Chemistry", *Can. Met. Quart.,* 29:1, pp. 1-12.

Papangelakis, V.G., and Demopoulos, G.P., 1990, "Acid Pressure Oxidation of Arsenopyrite: Part II: Reaction Kinetics", *Can. Met. Quart.,* 29:1, pp. 13-20.

Pinches, A., 1975, "Bacterial Leaching of an Arsenic-bearing Sulphide Concentrate", in *Leaching and Reduction in Hydrometallurgy,* A.R. Burkin (Editor), Institution of Mining and Metallurgy, London, England, pp. 28-35.

Raudsepp, R., and Beattie, M.J.V., 1985, "Arsenic and Iron control in the Arseno Process", in *Impurity: Control and Disposal,* 15th Annual Hydrometallurgical Meeting, Vancouver, Canada, paper 9.

Ruitenberg, R., Hansford, G.S., Reuter, M.A., and Breed, A.W., 1999, "The Ferric Leaching Kinetics of Arsenopyrite", *Hydrometallurgy,* 52, pp. 37-53.

Sedelnikova, G.V., Aslanukov, R.Ya., and Savari, E.E., 1999, "Study of the Conditions of Forming Environmentally Sound Insoluble Arseniferrous Products in the Course of Biohydrometallurgical Processing of Gold-arsenic Concentrates", in *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century,* Proceedings of the International Biohydrometallurgy Symposium IBS'99, Part B: Molecular Biology, Biosorption, Bioremediation, R. Amils and A. Ballester (Editors), San Lorenzo de El Escorial, Madrid, Spain, pp. 769-778.

Shengming, X., Jintong, X., and Chuanfu, Z., 1998, "Kinetics of Ferric Chloride Leaching of High Arsenic-Bearing Silver-Gold Concentrate", in *ICHM'98: Proceedings of the Third International Conference on Hydrometallurgy",* Y. Xianwan, C. Qiyuan and H. Aiping (Editors), The Nonferrous Metals Society of China, Kunming, China, pp. 125-129.

Shengming, X., Qonglin, L., Guoli, S., and Riqin, Y., 1998, "A Novel Technology for Leaching Gold From Silver-Gold Concentrate Bearing Arsenic by Hydro-treatment and Cyanidation", in *ICHM'98: Proceedings of the Third International Conference on Hydrometallurgy",* Y. Xianwan, C. Qiyuan and H. Aiping (Editors), The Nonferrous Metals Society of China, Kunming, China, pp. 578-582.

Spencer, P.A., and Budden, J.R., 1990, "Metallurgical Considerations in the Design of a Bio-oxidation Plant: A Case Study for a refractory Arsenopyrite Concentrate", in *EPD Congress '90,* D.R. Gaskell (Editor), TMS, Anaheim, CA, pp. 295-303.

Spencer, P.A., Budden, J.R., and Barrett, J., 1991, "Pilot-plant Bio-oxidation of Gold-bearing Arsenopyrite Concentrates", *Trans. Instn. Min. Metall. (Sect. C),* 100, pp. C21-C24.

Stefanakis, M., Hassapis, J., and Demetriades, D., 1988, "Dearsenifying Roasting and Extraction from a Refractory Pyrite Concentrate", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 173-197.

Stefanakis, M., and Kontopoulos, A., 1990, "Arsenic Fixation and Tailings Disposal in METBA'S Gold Project", in *Sulphide Deposits –Their Origin and Processing,* P.M.J. Gray et al. (Editors), IMM, London, England, pp. 289-300.

Vaughan, J.R., Dunne, R.C., and Bacigalupo-Rose, S., 1992, "Mineralogical Aspects of the Treatment of Arsenical Gold Ores", in *Innovations in Gold and Silver Recovery,* Randol, pp. 3011-3012.

Wei, S., Linrong, W., Taozhi, T., Zhaoheng, F., and Guangxiang, X., 1998, "Pretreatment of Arsenic-Bearing Refractory Gold Ores by Ammonia Leching", in *ICHM'98: Proceedings of the Third International Conference on Hydrometallurgy",* Y. Xianwan, C. Qiyuan and H. Aiping (Editors), The Nonferrous Metals Society of China, Kunming, China, pp. 208-212.

Wright, K.P., 1961, "Fluid Bed Roasting Practice in the Red Lake Camp", *CIM Bulletin,* 54:592, pp. 595-600.

5.3 From Cobalt Concentrates

Schaufelberger, F.A., "Leaching of Arsenide Ores", *US Patent Office, N° 2,805,936,* September 10, 1957.

5.4 From Arsenic-containing Copper Smelter Dusts

Anderson, C. G., 1984, ., "A Survey of Techniques to Remove Arsenic and Antimony from Copper Smelter Flue Dust", *M. Sc. Thesis*, Montana Tech College Min. Sci. Tech., Butte, MT, 126 p.

Conner, J.R., 1990, *Chemical Fixation and Solidification of Hazardous Wastes,* Van Nostrand Reinhold, New York.

Derka, J.R., 1993, "Methods of Recovering Arsenic Values from Waste", *Canadian Patent: 1314149.*

Dong, S.L., 1994, "An Investigation on Hydrometallurgical Processing of Arsenic Sulfide Residues", *Sulfuric Acid Industry,* 5, pp. 3-8.

Downey, J.P., and Mudgett, H., 1997, "Process for Stabilization of Arsenic", *Canadian Patent: 2247098.*

E&MJ, 1987, "Cashman Process may offer key to Treating Arsenical Ores", 188:11, p. 55.

Eriksson, B.S., and Petersson, S.A., 1983, "Method for Working-Up Arsenic-Containing Waste Products", *Canadian Patent: 1154971.*

Filippou, D., and Demopoulos, G.P., 1997, "Arsenic Immobilization by Controlled Scorodite Precipitation", *JOM,* 49:12, pp. 52-55.

Geldart, J., Williamson, R., and Maltby, P., 1992, "Aqueous Pressure Oxidation as a Waste Treatment Process – Stabilizing Roaster Wastes", in *Hydrometallurgy, Theory and Practice,* Part B, Volume 30, W.C. Cooper and D.B. Dreisinger (Editors), pp. 29-44.

Giles, D.E., and Boden, a., 1977, "Hydrometallurgical Treatment of Port Kembla Copper-Smelter Dust", *Proc. Aus. Inst. Min. Met.,* 262 (June), pp. 39-47.

Harris, G.B., and Krause, E., 1993, "The Disposal of Arsenic from Metallurgical Processes: Its Status Regarding Ferric Arsenates", in *Extractive Metallurgy of Nickel, Cobalt,* Vol. 1, Fundamental Aspects, R.G. Reddy and R.N. Weizenbach (Editors), TMS Annual Meeting, Colorado, pp. 1221-1237.

Harris, G.B. and Monette, S., 1985, "A Hydrometallurgical Approach to Treating Copper Smelter Precipitator Dusts", in *Complex Sulphides: Processing of Ores, Concentrates and By-Products,* A.D. Zunkel, R.S. Boorman, A.E. Morris and R.J. Wesely (Editors), TMS-AIME, San Diego, CA, pp. 361-375.

Herbert, J., and Boischot, P., 1948, "Fixation of Arsenic by Calcium Carbonate", *Compt. Rend.,* 226, pp. 747-749.

Hopkin, W., 1988, "The Problem of Arsenic Disposal in Nonferrous Metals Extraction", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 363-384.

Ke, J., and Qin, R., 2000, "Arsenic Removal and Bismuth Recovery from Copper Smelter Flue Dust", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 293-298.

Knoepke, J.R., 1974, "Treatment of Copper Dross Flue Dust for the Extraction of Arsenic", *M. Sc. Thesis,* Montana Tech College Min. Sci. Tech., Butte, MT.

Kondo, Y., 1980, "Recovery and Fixation of Arsenic from Metallurgical Intermediates", in *MMIJ-AIME 4th Joint Meeting,* Tokyo, Japan, pp. 45-58.

Kunter, R.S., and Bedal, W.E., 1991, "The Cashman Process Treatment of smelter Flue Dusts and Residues", in *Residues and Effluents – Processing and Environmental Considerations,* R.G. Reddy, W.P. Imrie, and P.B. Queneau (Editors), TMS, San Diego, CA, pp. 269-282.

Litz, J.E., "Flue Dusts: An Ideal Feed Resource Recovery", 1992, in *Residues and Effluents – Processing and Environmental Considerations,* R.G. Reddy, W.P. Imrie, and P.B. Queneau (Editors), TMS, San Diego, CA, pp. 223-238.

Ma, T.X., 1990, "Introduction of Treatment of Arsenic Sulfide Residues in Guixi Smelter", *Jiangxi Copper engineering,* 4, pp. 32-37.

Mavhingawuta, N.C., and Broadbent, C.P., 1994, "Incorporation of Arsenic in Silicate Slags as a Disposal Option", *Trans. Instn. Min. Metall. (Sect. C),* 103, pp. C1-C8.

Mehta, A.K., 1978, "Fixation of Arsenic in Copper Smelter Flue Dust", *M. Sc. Thesis*, Montana Tech College Min. Sci. Tech., Butte, MT, 89 p.

Mehta, A.K., 1981, "Investigations of New Techniques for Control of Smelter Arsenic Bearing Wastes", *Project Summary,* US EPA, Report: EPA-600/S2-81-049, Industrial Enviromental Research Laboratory, Cincinnati, OH.
Page web: www.p2pays.org/ref/02/01749.pdf

Peterson, M.R., 1985, "Removal of Arsenic and Recovery of Metal Values From Lead Smelter Speiss", *M. Sc. Thesis*, Montana Tech College Min. Sci. Tech., Butte, MT, 79 p.

Sández, M., Robles, A., and Serna, E., 1999, "Alternativa de Tratamiento de los Polvos Generados en hornos Eléctricos", in *Congreso Internacional de la AIMMG,* Acapulco, México.

Sández, M., Robles, A., and Serna, E., 1999, "Alkaline Arsenic Leacginh From Smelter Flue Dust and Leaching Solution Regeneration", in *Copper 99-Cobre 99 International Conference,* Volume VI: Smelting, Technology Devepment, Process, Modeling and Fundamentals, C. Díaz, C. Landolt and T. Utigard (Editors), TMS, Phoenix, AZ, pp. 261-272.

Southwick, L.M., 1998, "The Regulatory Ecouragement of Metals Recycling – Vete a Otro Perro Con Ese Hueso", *JOM*, 50:7.

Taschereau, C.A., 1998, "Le Problème de l'arsenic dans les Résidus Miniers: Le Cas de la Mine Chimo", *Mémoire Maître ès Sciences (M.Sc.),* Département de mines et métallurgie, Université Laval, Québec, Canada.

Tozawa, K., Umetsu, Y., and Nishimura, T., 1979, "A Hydrometallurgical Treatment of Arsenic Bearing Intermediate Products in Smelters", *Bull. Res. Inst. Min. Dress. Met.,* Tohoku University, 25:1, pp. 127-135.

Twidwell, L.G., and Mehta, A.K., 1985, "Disposal of Arsenic Bearing Copper Smelter Flue Dust", *Nuclear Chem. Waste Management,* 5, pp. 297-303.

Valenzuela, A., Fytas, K., and Sánchez, M., 2000, "Arsenic Management in Pyrometallurgical Processes, Part II: Recovery and Disposal", in *V International Conference on Clean Technology for the Mining Industry,* Vol. II: Environmental Improvements in Mineral Processing and Extractive Metallurgy, M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile.

Vircikova, E., Ludovit, M., and Pavol, P., 1999, "Methods of Arsenic Waste Treatment and Disposal – Case Studies", *Rewas'99: Global Symposium on Recycling, Waste treatment and Clean Technology*, Vol. I, I. Gaballah, J. Hager and R. Solozabal (Editors), Spain, pp. 65-73.

Wang, H., Jiant, K., and Li, L., 1999, "Oxidative Pressure Leaching for Arsenic Sulfide Residues from Gas Cleaning of Copper Smelting", in *Proc. Global Conference on Environmental and Metallurgy*, Q. Dingfan and Ch. Youyi (Editors), Beijing, China, Int. Academic Publishers, pp. 401-405.

5.5 From Arsenic-containing Solutions

Ball, B.R., and Brix, K.V., 2000, "Passive Treatment of Metalloids Associated with Acid Rock Drainage", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi*, C. Young (Editor), SME, Littleton, CO, pp. 95-104.

Bothe, Jr., J.V., and Brown, P.W., 1999, "Arsenic Immobilization by Calcium Arsenate Formation", *Environ. Sci. Technol.*, 33, pp. 3806-3811.

Castro, S.H., Vergara, F., and Sánchez, M.A. (Editors), Effluent Treatment in the Mining Industry, University of Concepción, Chile, 1998.

Cohen, J.M., 1983, "Extraction of Antimony and Arsenic from Copper Refining Electrolyte", in *International Solvent Extraction Conference*, AICHE, Denver, CO, pp. 222-223.

Comba, P., 1987, "Removal of Arsenic From Process and Wastewater Solutions", *M. Sc. Thesis*, Montana Tech College Min. Sci. Tech., Butte, MT, 137 p.

Das, R.P., and Anand, S., 1999, "Precipitation of Arsenic in the $Fe(II)-NH_3-(NH_4)_2SO_4-O_2$ System", *Hydrometallurgy*, 53, pp. 267-277.

Decarlo, E.H., and Zeitlin, H., 1981, "Simultaneous Separation of Trace Levels of Germanium, Antimony, Arsenic and Selenium from an Acid Matrix by Adsorbing Colloid Flotation", *Anal. Chem.*, 53, pp. 1104-1107.

Demopoulos, G.P., Droppert, D.J., and Van Weert, G., 1995, "Precipitation of Crystalline Scorodite ($FeAsO_4 \cdot 2H_2O$) from Chloride Solutions", *Hydrometallurgy*, 38, pp. 245-261.

Demopoulos, G.P., 1996, "Effluent Treatment by Crystallization", in *Clean Technology for the Mining Industry*. M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile, pp. 1-24.

Domville, S.J., and Henry, G., 1995, "Improved Process for Treatment of Mill Effluent Containing Arsenic and Cyanide", in *Innovations in Gold and Silver Recovery*, Randol, pp. 8689-8693.

Droppert, D.J., Demopoulos, G.P., and Harris, G.B., 1996, "Ambient Pressure Production of Crystalline Scorodite from Arsenic-rich Metallurgical Effluent Solutions", in *EPD Congress 1996,* G.W. Warren (Editor), TMS, Tuscaloosa, AL, pp. 227-239.

Dutré, V., and Vandecasteele, C., 1995, "Solidification/Stabilisation of Hazardous Arsenic Containing Waste from a Copper Refining Process, *J. Hazardous Materials,* 40:1, pp. 55-68.

Fuentes, G.E., 1999, "Arsenic Extraction from Contaminated Sulphuric Acid", in *29th Annual Hydrometallurgical Meeting,* Proceeding of the International Symposium on Solid/Liquid Separation, including Hydrometallurgy and the Environment, G.B. Harris and S.J. Omelon (Editors), Québec City, Canada, pp. 343-353.

Fytas, K., and Taschereau, C., 2000, "Arsenic Problems in Mine Tailings", in *SWEMP 2000,* Sixth International Symposium on Environmental Issues and Waste Management in Energy and Mineral Production, R.K. Singhal (Editor), Calgary, Alberta.

Gale, M., 1998, "Removal of Arsenic From Wastewaters by Calcium/Arsenic/Phosphorous and Iron/Arsenic/Phosphorous Precipitation", *M. Sc. Thesis*, Montana Tech of The University of Montana, Butte, MT.

Hollo, J., et al., 1968, "Removal of Arsenic from Industrial Waste Water", *Periodica Polytech.,* 12:3, pp. 283-292.

Isaacson, A.E., and Jeffers, T.H., 1995, "Arsenic Removal from Dilute Waste Streams", in *New Remediation Technology in the Changing Environmental Arena,* Society for Mining, Metallurgy and Exploration, Littleton, CO, pp. 217-221.

Jdid, E., Blazy, P., and Elamari, K., 1997, "Arsenic Removal and Copper Recycling From Copper Refinery Anodic Slimes by Sulphuric Acid Leaching", in *Proceedings of the XX International Mineral Processing Congress,* Volume 4: Solid-liquid Separation, Hydro- and Biohydrometallurgy, H. Hoberg and H. von Blottnitz (Editors), Aachen, Germany, pp. 209-215.

Junghanss, H., et al., 1975, "Precipitation and Separation of Arsenic from Copper Containing Solutions", *German Patent: 2,342,729.*

Jurado, K.R., Zambrano, C., and Lama, C., 2000, "On Line Control Optimization to Remove Arsenic from Weak Acid Effluents", in *V International Conference on Clean Technology for the Mining Industry,* Vol. I: Waste Treatment and Environmental Impact in the Mining Industry, M. A. Sánchez, F. Vergara and S.H. Castro (Editors), University of Concepción, Chile.

Kabanova, L.M., and Ponomarev, V.D., 1956, "The precipitation of Arsenic from Solutions of Zinc and Cadmium Sulfates", *Trudy Altaisk. Gorno-Met. Naush. – Issled. Inst.,* 3, pp. 136-156.

Klamp, G., and Wanner, D., 1991, "Removal of Arsenic From Washing Acid by the Sachtleben-Lurgi Process", in *Residues and Effluents – Processing and Environmental Considerations,* R.G. Reddy, W.P. Imrie and P.B. Queneau (Editors), TMS, San Diego, CA, pp. 833-837.

Kobayashi, M., and Koyama, K., 1998, "Recovery of Harmful Selenium and Arsenic Using Aqueous Processing for Environment Conscious Process", in *EPD Congress 1998,* B. Mishra (Editor), TMS Annual Meeting, San Antonio, TX, pp. 25-37.

Kontopoulos, A., Stefanakis, M., and Papassiopi, N., 1988, "Arsenic Control in Hydrometallurgy by Precipitation as Ferric Arsenates", in *Proceedings of the First International Conference on Hydrometallurgy",* The Nonferrous Metals Society of China, Beijing, China, pp. 672-677.

Lawrence, R.W., and Higgs, T.W., 1999, "Removing and Stabilizing As in Acid Mine Water", *JOM,* 51:9, pp. 27-29.

Lihme, I.P., 1919, "Lead Arsenate", *US Patent: 1,302186.*

Misra, M., Nanor, J., and Bucknam, C.H., 2000, "Enhanced Precipitation and Stabilization of Arsenic from Gold Cyanidation Process", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 141-148.

Miyamoto, O., Suginohara, Y., and Yanagase, T., 1975, "Removal of arsenic from Waste Water: Treatment with MnO_2 and Separation of As from the Precipitate, *J. Min. Met. Inst. Japan,* 91, pp. 33-38.

Nishimura, T., Wang, Q., and Umetsu, Y., 1996, "Removal of Arsenic from Process Liquors by Oxidation of Iron(II), Arsenic(III) and Sulfur(IV) with Oxygen", in *Iron Control and Disposal,* Proceedings of the Second International Symposium on Iron Control in Hydrometallurgy, J.E. Dutrizac and G.B. Harris (Editors), CIM, Ottawa, Canada, pp. 535-548.

Papassiopi, N., Virčíková, E., Nenov, V., Kontopoulos, A., and Molnár, L., 1996, "Removal and Fixation of Arsenic in the Form of Ferric Arsenates. Three Parallel Experimental Studies"; *Hydrometallurgy,* 41, pp. 243-253.

Papassiopi, N., Stefanakis, M., and Kontopoulos, A., 1988, "Removal of Arsenic From Solutions by Precipitation as Ferric Arsenates", in *Arsenic Metallurgy Fundamentals and Applications,* R.G. Reddy, J.L. Hendrix and P.B. Queneau (Editors), TMS Annual Meeting and Exhibition, Phoenix, AZ, pp. 321-334.

Petrosyants, S.A., et al., 1971, "Removal of an Arsenic Impurity from Zinc Sulfate Solutions During Leaching", *Izy. Vyssh. Ucheb. Zaved., Tsvet. Met.,* 14:4, pp. 20-22.

Plessas, K., 1993, "Arsenic Removal From Process and Waste Water Solutions". *M. Sc. Thesis*, Montana Tech College Min. Sci. Tech., Butte, MT, 103 p.

Qiankun, W., and Demopoulos, G.P., 1998, "A Novel Hydrometallurgical Process for the Immobilization of Arsenic", in *ICHM'98: Proceedings of the Third International Conference on Hydrometallurgy",* Y. Xianwan, C. Qiyuan and H. Aiping (Editors), The Nonferrous Metals Society of China, Kunming, China, pp. 543-553.

Redmon, C.L., Subbanna, S.N., and Smith, R.A., 1994, "Process for Separating Arsenic Acid from Aqueous Mixture Comprising Sulfuric and Arsenic Acids", *Canadian Patent: 2155949.*

Riches, G.R., and Piver, W.C., "Lead Arsenate", *Canadian Patent: 191,628,* July 1919.

Rosehart, R.G., and Lee, J., 1972, "Effective Methods of Arsenic Removal from Gold Mine Wastes", in *Proceedings of the Fourth Annual Meeting of the CMP,* CIM, pp. 107-128.

Scott, J.S., 1989, "An Overview of Gold Mill Effluent Treatment", in *Proceedings, Gold Mill Effluent Treatment Seminars,* Environment Canada, Ottawa, pp. 1-22.

Sharova, A.K., and Ketova, E.N., 1968, "Separation of Arsenic from Solution by Precipitating Titanium Arsenate", *Akad. Nauk. SSR. Ural. Fil., Trudy Inst. Khim.,* 17, pp. 130-133.

Teixeira, L.A., Monteiro, A.G., and Kohler, H.M., 1990, "The Detoxification of Effuents Containing Arsenic with Iron Sulphate and Hydrogen Peroxide", in *EPD Congress '90,* D.R. Gaskell (Editor), TMS-AIME, Anaheim, CA, pp. 189-207.

Tozawa, K., Nishimura, T., Akahori, M., Malaga, M.A., 1992, "Comparison Between Purification Processes for Zinc Leach Solutions with Arsenic and Antimony Trioxides", in *Hydrometallurgy, Theory and Practice,* Part B, Volume 30, W.C. Cooper and D.B. Dreisinger (Editors), pp. 445-461.

Trelles, R.A., and Amato, F.D., 1949, "Treatment of Arsenical Waters with Lime", *Rev. Obras Sanit. Nación,* Buenos Aires, 13, pp. 95-96.

Twidwell, L.G., Plessas, K.O., and Bowler, T.P., 1993, "Removal of Arsenic from Wastewaters and Stabilization of Arsenic Bearing Waste Solids", in *Mercury and Arsenic Wastes: Removal, Recovery, Treatment, and Disposal,* Pollution Technology Review N° 214, US EPA (Editor), NJ, pp. 105-109.

Wang, Q., Nishimura, T., and Umetsu, Y., 2000, "Oxidative Precipitation for Arsenic Removal in Effluent Treatment", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 39-52.

Wang, Q., Demopoulos, G.P., and Harris, G.B., 2000, "Arsenic Fixation in Metallurgical Plant Effluents in the Form of Crystalline Scorodite via a Non-Autoclave Oxidation-Precipitation Process", in *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi,* C. Young (Editor), SME, Littleton, CO, pp. 225-238.

Wasay, SA., Haron, M.D., Uchiumi, A., and Tokunaga, S., 1995, "Removal of Arsenite and Arsenate Ions From Aqueous Solution by Basic Yttrium Carbonate", *Water Research*, 30:5, pp. 1143-1148.

Weir, D.R., and Master, I.M., "Removal of Arsenic from Aqueous Solutions", *Canadian Patent 358,966,* August 1980.

Wilson, S.R, 1998, "Removal of Arsenic From ASARCO Acid Plant Blowdown Water as Stable, Storable Precipitates", *M. Sc. Thesis*, Montana Tech of The University of Montana, Butte, MT.

Wódka, J., Charewicz, W.A., and Janicki, T., 1999, "Pressure Reduction of Copper (II) from Highly Acidic Aqueous Solutions Containing Arsenic", *Hydrometallurgy,* 52, pp. 177-187.

Yanagase, T., "Removal of Arsenic Contained in Geothermal Hot Water with a Use of Titanium Hydroxide", *Report of Special Project Research on Energy,* Japan Ministry of Education, Science and Culture, SPEY 8, pp. 423-430.

Yun, L., 1998, "Precipitation of Manganese Arsenate", in *ICHM'98: Proceedings of the Third International Conference on Hydrometallurgy",* Y. Xianwan, C. Qiyuan and H. Aiping (Editors), The Nonferrous Metals Society of China, Kunming, China, pp. 120-124.