BACKGROUND REPORT

AP-42 SECTION 12.3

PRIMARY COPPER SMELTING

Prepared for

U.S. Environmental Protection Agency OAQPS/TSD/EIB Research Triangle Park, NC 27711

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1.0 INTRODUCTION

The document "Compilation of Air Pollutant Emission Factors" (AP-42) has been published by the U.S. Environmental Protection Agency (EPA) since 1972. Supplements to AP-42 have been routinely published to add new emission source categories and to update existing emission factors. AP-42 is routinely updated by the EPA to respond to new emission factor needs of the EPA, state and local air pollution control agencies, and industry.

An emission factor relates the quantity (weight) of pollutants emitted to a unit of activity of the source. The uses for the emission factors reported in AP-42 include:

- 1. Estimates of area-wide emissions;
- 2. Emission estimates for a specific facility; and
- 3. Evaluation of emissions relative to ambient air quality.

The purpose of this report is to provide background information for the revision of AP-42 Section 12.3 *Primary Copper Smelting*.

Including the introduction (Chapter 1), this report contains four chapters. Chapter 2 gives a description of the secondary copper industry. It includes a characterization of the industry, an overview of the different process types, a description of emissions, and a description of the technology used to control emissions resulting from processing zinc scrap.

Chapter 3 is a review of emissions data collection and analysis procedures. It describes the literature search, the screening of emission data reports, and the quality rating system for both emission data and emission factors. Chapter 4 details criteria and noncriteria pollutant emission factor development. It includes the review of specific data sets and the results of data analysis.

2.0 INDUSTRY DESCRIPTION

2.1 General

As of 1992, more than half of the approximately 1.6 million megagrams (1.8 million tons) of copper produced annually in the U.S. is processed by the nation's eight primary smelters. Most of this copper is further refined into relatively pure metallic copper or is alloyed with zinc or tin to form brass or bronze. An increasingly important alternative to conventional copper smelting and refining is solvent extraction/electrowinning (SX-EW) technology, in which dilute sulfuric acid is percolated through copper-bearing ore to leach out the copper. The copper is concentrated through solvent extraction, and is subsequently recovered by plating onto a starter cathode in a process called electrowinning. SX-EW capacity in the U.S. was 358,000 megagrams (395,000 tons) in 1989. The SX-EW process is an alternative to smelting, but it and its emission streams are fundamentally different from smelting, and as such it will not be addressed in detail in this document. It is worth noting, however, that a study performed by the National Institute of Occupational Safety and Health (NIOSH) revealed significant workplace concentrations of sulfuric acid mist at an SX-EW facility in Arizona.

Refined copper and copper alloys are valuable for their electrical and thermal conductivity and their resistance to corrosion. They are used in construction, electrical and electronic applications, and industrial machinery, as well as a variety of smaller applications. The operator, location, approximate annual capacity, and processes of each of the eight primary copper smelters in the U.S. are listed in Table 2.1-1.

2.2 Process Description

Copper is mined from a variety of ores, often containing less than one percent copper. This copper is typically in the form of mineral compounds with sulfur, iron, arsenic, and tin. To facilitate transportation to smelters, concentration to about 30 percent copper content is accomplished at the mine sites via crushing, grinding, and flotation. The resulting "concentrate" is processed in a reverberatory furnace, an electric furnace, or one of several relatively new oxygen-enriched flash smelting furnaces to yield "matte" of as much as 65 percent copper content. The iron in this matte is oxidized in a converter to

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Operator	Location	1992 Capacity ^b	Type of Smelting Process
ASARCo, Inc.	Hayden, Arizona	170	
Chino Mines Co.	Hurley, New Mexico	170	Inco Flash
Cyprus Miami Co.	Globe, Arizona	180	Isasmelt/Electric
Kennecott Corp.	Garfield, Utah	210	Noranda Modified
Magma Copper Co.	San Manuel, Arizona	290	
Phelps Dodge Corp.	Hidalgo, New Mexico	190	Outokumpu Flash
ASARCO, Inc.	El Paso, Texas	104	
Copper Range Co.	White Pine, Michigan	60	Reverberatory

Table 2.1-1: Primary Copper Smelters^a

a) Reference 3

b) 1992 annual design capacity in thousands of megagrams of blister or anode copper

produce "blister" copper of 97 to 98.5 percent purity, which can then be further refined pyrometallurgically and/or hydrometallurgically.

Before introduction into traditional reverberatory furnaces, concentrates are often roasted to reduce impurities such as sulfur, antimony, arsenic, and lead. The roasted product, calcine, serves as a dried and heated charge for the smelting furnace. However, reverberatory furnaces account for only 12 percent of U.S. primary smelting capacity as of 1992, and the larger of the two reverberatory furnaces (ASARCo, El Paso, TX) is scheduled to be replaced in 1993 by a continuous top-blowing (Contop) process flash smelter. The remaining smelter utilizing reverberatory furnace technology, Copper Range Co. in White Pine, MI, uses unroasted (green)

concentrate as feed to its furnace. As a result, the concentrate roasting process is essentially obsolete at U.S. primary copper smelting facilities.

The traditional *reverberatory* smelting process as it exists in the U.S. involves the charging of concentrate and a siliceous flux to an externally fired smelting furnace maintained at a temperature as high as 1500° C (2730° F). Impurities in the charge oxidize with the flux to form a layer of "slag," which floats on top of the molten matte, and much of the sulfur in the charge is released as sulfur dioxide (SO₂). The slag is frequently skimmed, and the matte is periodically tapped. Heat required for the melting process comes from partial oxidation of the sulfide charge as well as the burning of external fuel. The reverberatory furnace smelting operation is a continuous process.

Electric arc smelting furnaces generate heat with carbon electrodes that are lowered through the furnace roof and submerged in the slag layer of the molten bath. The feed consists of dried concentrates or calcine. The chemical and physical changes occurring in the molten bath are similar to those occurring in the molten bath of a reverberatory furnace. The matte tapping and slag skimming practices are also similar.

Flash furnace smelting consists of blowing fine, dried copper sulfide concentrates and silica flux with air, oxygen-enriched air, or oxygen blast into a hearth-type furnace maintained at approximately $1200^{\circ}C$ ($2200^{\circ}F$). Entry of these materials into the hot furnace causes the sulfide minerals (e.g., CuFeS₂) of the concentrate to react rapidly with the oxygen of the blast. This leads to the controlled oxidation of the iron and sulfur in the concentrate, a large evolution of thermal energy, and the melting of the solids. The products of flash furnaces are matte of 45 to 65 percent copper, molten slag containing iron oxides plus gangue and flux oxides, and offgas. The slag typically contains as much as two percent copper. This slag can be recycled to the flash furnace, or its copper content can be recovered in a slag cleaning furnace, often electric. The flash furnace offgas contains anywhere from 10 to 80 percent by volume sulfur dioxide (SO₂). In all domestic copper smelting facilities utilizing flash smelting technology, the valuable thermal energy in this gas is recovered in a waste heat boiler, and the SO₂ is converted into sulfuric acid. One facility in Canada compresses the SO₂ into liquid form, while a facility in Eastern Europe reduces the SO₂ to elemental sulfur. Approximately 3 to 15 percent of the furnace charge exits the furnace as dust in the offgas, primarily in the form of oxidized concentrate which has not settled out earlier. This dust is captured in a gas cleaning train, usually consisting of electrostatic precipitators, and is recycled to the furnace for copper recovery.

The two types of flash furnaces currently in operation in the U.S. are Outokumpu furnaces and Inco furnaces. These furnace types represent 35 and 25 percent of U.S. primary copper smelting capacity, respectively. Both furnaces are constructed mainly of chromia-magnesia bricks (MgO and Cr_2O_3 -MgO) surrounded by a steel shell. Because the concentrate feed to these flash furnaces must be dry for reasons that will be discussed below, rotary, flash, fluidized-bed, and spray dryers are used in conjunction with these furnaces to obtain a feed containing no more than 0.2 percent water by mass.

The Outokumpu flash smelting furnace is characterized by five major components:

- concentrate burners, which combine dry particulate feed with oxygen-bearing blast and direct the mixture in suspension form downward into the furnace;
- a reaction shaft where most of the reaction between oxygen and sulfide feed particles takes place;
- a settler where molten matte and slag droplets collect and form separate layers;
- an off-take for removing SO_2 -bearing gases from the furnace; and
- tapholes near the bottom of the furnace for removing matte and slag.

A cutaway view of a typical Outokumpu flash furnace is illustrated in Figure 2.2-1. Crucial to the efficient operation of these furnaces are the creation of a good particle-gas suspension and the maintenance of a steady flow of feed materials into the furnace. These conditions can only be obtained through the use of dry feed concentrate. To maintain thermal balance in this suspension, the blast is preheated with direct-fired burners; these burners will use much more fuel if the furnace is operating with an air blast than if it is operating with an oxygen blast. While the smelting process is continuous, tapping of matte and slag are intermittent. Matte is tapped into ladles for transport to converters, and slag is either tapped into a cleaning furnace for copper recovery or is dried and recycled into the flash furnace with ore concentrate.

Inco flash smelting consists of blowing industrial oxygen and dry concentrate horizontally into a hearth-type furnace. A cutaway view of a typical Inco flash furnace is illustrated in Figure 2.2-2. The principal advantage of Inco furnaces over Outokumpu furnaces is compactness, which enable them to be used to replace existing reverberatory furnaces. The reactions taking place are

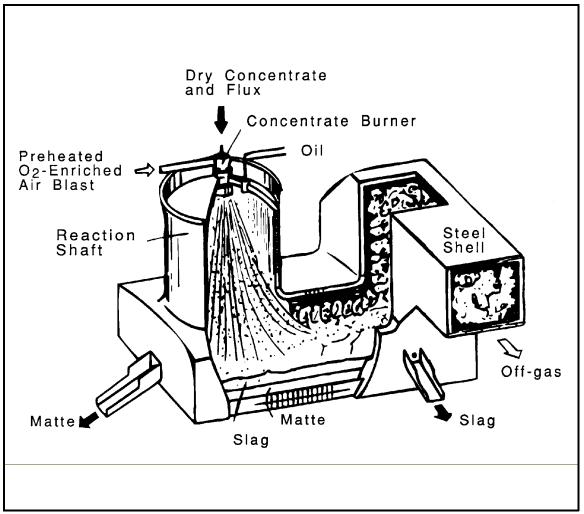


Figure 2.2-1: Cutaway View of Outokumpu Flash Furnace.

similar to those in an Outokumpu furnace, but without the benefit of fossil fuel combustion. This type of furnace is characterized by three major components:

- concentrate burners, two at each end of the furnace, through which ambienttemperature oxygen, concentrate, and flux are blown into the furnace;
- a central gas off-take through which the offgas is withdrawn for delivery to the cooling, dust removal, and SO₂ fixation systems; and
- matte and slag tapholes through which the liquid products are periodically removed from the furnace.

As with Outokumpu furnaces, maintenance of good gas/particle suspension and steady flow into the furnace are essential to efficient operation of these units. The primary differences in

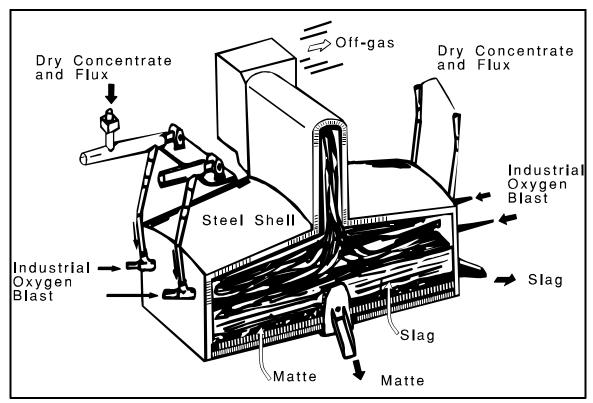


Figure 2.2-2: Cutaway View of Inco Flash Furnace.

operating conditions derive from the exclusive use of industrial oxygen and the reliance on sulfur and iron oxidation for thermal energy input. The volume of offgas is very small relative to Outokumpu furnaces, and SO_2 concentrations are much higher (approximately 75 percent). External fuel combustion is required at Inco furnaces only during start-up periods, to bring the furnace chamber to its operating temperature. Slag produced at Inco flash furnaces typically contains no more than one percent copper, thereby eliminating the cost of slag cleaning equipment necessary to attain similar copper recovery efficiencies with Outokumpu furnaces. The offgases from Inco furnaces are typically not routed through waste heat boilers, but rather proceed to dust settling chambers and gas cleaning systems. Dust recovery of 99.99 percent is achieved with various combinations of scrubbers, cyclones, and both wet and dry electrostatic precipitators. The Inco flash smelting furnace operated by Chino Mines Co. is able to maintain a consistent flow of constant strength gaseous SO_2 into its sulfuric acid plant by condensing some of the SO_2 in the offgas when the flow rate of this gas stream is higher than usual, and evaporating this stored liquid SO_2 when the flow rate is low. The *Noranda* process, as originally designed, allowed the continuous production of blister copper in a single vessel by effectively combining roasting, smelting and converting into one

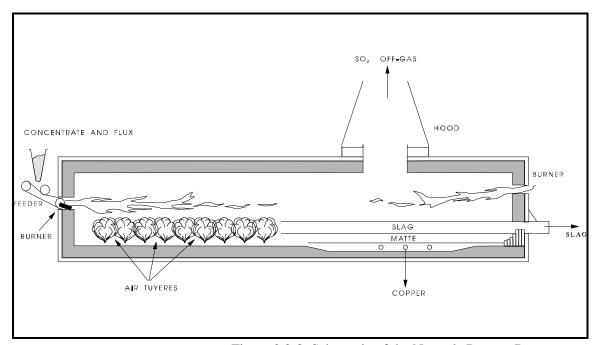


Figure 2.2-3 Schematic of the Noranda Process Reactor

operation. Metallurgical problems, however, have led to the operation of these reactors for the production of copper matte. The Noranda process uses heat generated by the exothermic oxidation of hydrogen sulfide. Additional heat is supplied by oil burners or by coal mixed with the ore concentrates. Figure 2.2-3 illustrates the Noranda process reactor.

Converting produces blister copper by eliminating the remaining iron and sulfur present in the matte. Most U.S. smelters use Pierce-Smith converters, which are refractory-lined cylindrical steel shells mounted on trunnions at either end, and rotated about the major axis for charging and pouring. An opening in the center of the converter functions as a mouth through which molten matte, siliceous flux, and scrap copper are charged and gaseous products are vented. Air, or oxygen-rich air, is blown through the molten matte. Iron sulfides are oxidized to form iron oxides (FeO, Fe₂O₃) and sulfur dioxide (SO₂). Blowing and slag skimming continue until an adequate amount of relatively pure Cu₂S, called "white metal," accumulates in the bottom of the converter. A final air blast ("final blow") oxidizes the copper sulfide to SO₂, and forms blister copper. The blister copper is removed from the converter for subsequent refining. The SO₂ produced throughout

the operation is vented to pollution control devices. An environmentally superior alternative to the use of Pierce-Smith converters is "flash converting," a process jointly developed by Kennecott Corporation and Outokumpu Oy of Finland but not currently employed by any U.S. primary copper smelting facilities. This process is similar to Outokumpu flash smelting with oxygen enriched air and dried, granulated matte as feed materials.

Impurities in blister copper may include gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, tellurium, tin, and zinc. Fire-refining and electrolytic refining are used to purify blister copper. In *fire-refining*, blister copper is usually mixed with flux and charged into the furnace, which is maintained at 1100°C (2010°F). Air is blown through the molten mixture to oxidize the copper and any remaining impurities, which are then removed as slag. The remaining copper oxide is then subjected to a reducing atmosphere. The fire-refined copper is then cast into anodes, for further purification by electrolytic refining.

Electrolytic refining separates copper from impurities by electrolysis in a solution containing copper sulfate (Cu_2SO_4) and sulfuric acid (H_2SO_4). The copper anode is dissolved, and subsequently deposited at the cathode. As the copper anode dissolves, metallic impurities precipitate and form a sludge. Cathode copper, 99.95 to 99.96 percent pure, is then cast into bars, ingots or slabs.

2.3 Emissions and Controls

Emissions from primary copper smelters are principally particulate matter and oxides of sulfur (SO_x) . Emissions are generated from the roasters, smelting furnaces, and converters. Fugitive emissions are generated during material handling operations. Copper and iron oxides are the primary constituents of the particulate matter, but other oxides such as arsenic, antimony, cadmium, lead, mercury and zinc, may also be present, along with metallic sulfates and sulfuric acid mist. Because of considerable quantities of sulfur in the ores in which copper is found, significant emissions of sulfur dioxide occur from various processes associated with primary copper smelting. Recovery of this SO_2 in the form of sulfuric acid is economically worthwhile, and the only primary copper smelting facility in the U.S. not producing sulfuric acid is Copper Range Co. in White Pine, MI. Fuel combustion products also contribute to emissions from multiple hearth roasters, reverberatory furnaces, and Outokumpu flash smelting furnaces.

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Offgases from roasters usually are treated in an ESP or a combination spray chamber/ESP system for particulate recovery. Alternatively, these gases can be combined with smelter furnace offgas prior to particulate collection. Overall, the hot ESP's remove only 20 to 80 percent of the total particulate (condensed and vapor) present in the gas. Cold ESP's may remove more than 95 percent of the total particulate present in the gas. Particulate collection systems for smelting furnaces are similar to those for roasters. Reverberatory furnace offgases are usually routed through waste heat boilers and low velocity balloon flues to recover large particles and heat, then are routed through an ESP or a combination spray chamber/ESP system for final particulate removal.

Emissions from Pierce-Smith converters result primarily from charging and pouring procedures, during which the converter mouth is outside the gas collection hood. Especially severe are gaseous emissions when the converter is being rotated between its three positions, because blowing must be continued during this rotation to prevent molten materials from flowing back into the tuyeres and damaging the air delivery system. To prevent the hood from binding to the converter with splashing molten metal, a gap exists between the hood and the vessel, resulting in fugitive gaseous emissions. Converter offgases that are captured are treated in ESP's to remove particulate matter before being routed to on-site sulfuric acid plants.

Remaining smelter operations process material containing very little sulfur, resulting in insignificant SO_2 emissions. Particulate may be emitted from fire-refining operations. Electrolytic refining emissions are negligible unless the sulfuric acid tanks are open to the atmosphere. Crushing and grinding systems used in ore, flux and slag processing also contribute to fugitive dust problems.

Use of a sulfuric acid plant to treat copper smelter effluent gas streams requires that particulate-free gas with a steady SO_2 concentration of at least three percent be maintained. Table 2.3-1 shows typical average SO_2 concentrations from the various smelter units. The operation of sulfuric acid plants is discussed in detail in AP-42 Section 5.17. Sulfuric acid plants also treat converter gas effluent. Reverberatory furnace effluent for operations utilizing calcine rather than green feed contains minimal SO_2 and is usually not vented to on-site sulfuric acid plants. Effluent from the other types of smelter furnaces contains higher concentrations of SO_2 and is typically treated in sulfuric acid plants before being vented. Double-contact acid plants collect from 98 to more than 99 percent of the SO_2 , with typical effluent concentrations at about 500 parts per million by volume (ppmv) SO_2 .

Unit	SO ₂ Concentration (Volume %)	
Multiple hearth roaster	1.5 - 3	
Fluidized bed roaster	10 - 12	
Reverberatory furnace	0.5 - 1.5	
Electric arc furnace	4 - 8	
Outokumpu flash furnace, Phelps Dodge, Hildalgo, NM ^b	22	
Inco flash furnace, Chino Mines, Hurley, NM ^c	70	
Continuous smelting furnace	5 - 15	
Pierce-Smith converter	4 - 7	
Hoboken converter	8	
Single contract H ₂ SO ₄ plant	0.2 - 0.26	
Double contact H ₂ SO ₄ plant	0.05	

TABLE 2.3-1Typical Sulfur Dioxide Concentrations inOffgases from Primary Copper Smelting Sources^a

a) Reference 6 unless otherwise noted.

b) Reference 4, Table 2.1.

c) Reference 4, Table 3.1.

2.4 Review of References for Chapter 2.0

The following sources were contacted in order to obtain the most up-to-date information on industrial processes, emission stream characterization, and control technology concerning the primary copper smelting industry:

U.S. Department of the Interior, Bureau of Mines, Washington, DC.

A series of telephone conversations with the copper specialist with this government agency assisted in locating primary copper smelters, and provided estimates of the capacities of these facilities. Much of the information presented in the revised AP-42 section concerning the properties and uses of copper and the primary copper industry as a whole is based upon two documents published by the Bureau of Mines (Reference 1: "Copper," <u>Mineral Commodities Summary 1992</u> and Reference 2: "Copper," <u>Minerals Yearbook 1989</u>), both of which examine this industry from a primarily commercial standpoint. In addition, the more detailed <u>Minerals Yearbook</u> provided brief descriptions of the processes utilized in primary copper smelting, which were also used in the revision of the AP-42 section.

D.H. Hill Library, North Carolina State University, Raleigh, NC.

A literature search was conducted at this research library in order to obtain more up-to-date information on primary copper smelting processes, particularly the flash smelting methods. The result of this search is Reference 4, <u>Flash Smelting: Analysis, Control and Optimization</u>. This book provides more current and technical descriptions of these methods than are available in environmentally-related literature.

U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety & Health (NIOSH), Cincinnati, OH.

This agency was contacted by telephone in order to ascertain whether any research had been performed concerning emissions of sulfuric acid mist from electrolytic nonferrous refining processes into either workplace or ambient atmosphere. A search of the computerized bibliographic database of occupational safety and health maintained by NIOSH yielded Reference 5, "Health Hazard Evaluation Determination Report HE-79-10-576, Cities Service Company, Miami, Arizona." Results of this study indicated significant but not excessive workplace concentrations of sulfuric acid mist in a primary SX-EW facility producing 15 tons per day of copper cathode.

Pinal County (AZ) Air Quality Control District, Florence, AZ.

This agency was contacted in an effort to obtain emission test results for the ASARCo, Magma, and Cyprus Miami primary copper smelters in Arizona. This request was deferred to the state agency, which handles all issues pertaining to these facilities.

Arizona Department of Environmental Quality, Office of Air Quality, Phoenix, AZ.

This agency was contacted in order to obtain emission test results for the Magma, Cyprus Miami, and ASARCo primary copper smelters in Arizona, and no response was received. The state of Arizona has no jurisdiction over the Cyprus roast/leach plant in Casa Grande, AZ, because it is situated on an Indian reservation.

Copper Range Co., White Pine, MI.

The environmental engineering staff at this facility were contacted by telephone and by mail in an effort to obtain general process information and results of recent emission testing. No response was received.

ASARCo Inc., El Paso, TX.

Engineering personnel at this facility were contacted by telephone and by mail in order to obtain general information on the continuous top-blowing (Contop) flash smelting technology being implemented to replace a long-standing reverberatory furnace operation. This Contop process is currently scheduled to come on-line mid-year in 1993, and emission testing will be performed shortly thereafter. A general description of the process was requested as soon as possible in order to incorporate this information into the section revision, and that the results of the start-up testing be forwarded as soon as they become available, for incorporation into future revisions. No response was received.

Phelps Dodge Corp., Hidalgo, NM and

Chino Mines Co., Hurley, NM.

The environmental coordinator at the first of these two facilities was contacted by telephone in an attempt to obtain any available emission test results. No response was received. The latter facility was contacted by telephone at a later date, and it was determined that Chino Mines is a subsidiary of Phelps Dodge and that the environmental coordinator contacted earlier at the Hidalgo facility should also be contacted to obtain emissions data for the Hurley facility.

Magma Copper Co., San Manuel, AZ.

The manager of environmental affairs at this facility was contacted by telephone in order to obtain the results of emission testing performed in 1988. No response was received.

2.5 **REFERENCES FOR CHAPTER 2**

- 1. J.L.W. Jolly, "Copper," <u>Mineral Commodity Summaries 1992</u>, U.S. Department of the Interior, Bureau of Mines, Washington, DC, 1992.
- 2. J.L.W. Jolly, "Copper," <u>Minerals Yearbook 1989</u>, U.S. Department of the Interior, Bureau of Mines, Washington, DC, 1990.
- Facsimile transmission from J.L.W. Jolly, U.S. Department of the Interior, Bureau of Mines, Washington, DC, to C.M. Campbell, Pacific Environmental Services, Inc., Research Triangle Park, NC, 4 November 1992.
- 4. W.G. Davenport and E.H. Partelpoeg, <u>Flash Smelting: Analysis, Control and Optimization</u>, Pergamon Press, Elmsford, NY, 1987.
- R.L. Ruhe and M. Donohue, "Health Hazard Evaluation Determination Report HE-79-10-576, Cities Service Company, Miami, Arizona," Hazard Evaluations and Technical Assistance Branch, NIOSH, U.S. Department of Health, Education, and Welfare, Cincinnati, OH, 1979.
- Evaluation of the Controllability of SO₂ Emissions from Copper Smelters in the State of <u>Arizona</u>, EPA Contract No. 68-02-1354, Pacific Environmental Services, Inc., Santa Monica, CA, June 1975.

3.0 GENERAL EMISSION DATA REVIEW AND ANALYSIS PROCEDURES

3.1 Literature Search and Screening

The first step of the investigation into emissions from the secondary copper smelting industry involved a search of available literature. This search included the following references:

- 1. AP-42 background files maintained by the Emission Factor and Methodologies Section. The references from which most of the emission factors presented in both the previous and revised versions of AP-42 Section 12.3 are derived were obtained from these files, and are summarized in Chapter 4.0 of this background report. Also obtained from these files was a 1975 report entitled Evaluation of the Controllability of SO₂ Emissions from Copper Smelters in the State of Arizona which was not cited as a reference in previous versions of the AP-42 section. This report was the source of a table in the previous and revised versions of this AP-42 section listing estimated sulfur dioxide concentrations in offgases from several primary copper smelting sources.
- "Locating and Estimating" reports published by the Emission Factor and Methodologies Section. None of the pollutants for which these reports have been compiled is emitted from primary copper smelting facilities, and thus no useful information was contained in these reports.
- 3. PM_{10} "gap filling" documents as listed below; none of these documents contained data of a quality suitable for development of emission factors.
 - "PM₁₀ Emission Factor Listing Developed by Technology Transfer" (EPA-450/4-89-022).
 - "Gap Filling PM₁₀ Emission Factors for Selected Open Area Dust Sources" (EPA-450/88-003).
 - "Generalized Particle Size Distributions for Use in Preparing Size
 Specific Particulate Emission Inventories" (EPA-450/4-86-013).
- Handbook of Emission Factors, Parts I and II, Ministry of Health and Environmental Protection, The Netherlands, 1980/1983. No information concerning the primary copper smelting industry is contained in this handbook.

- 5. The EPA databases, including but not limited to the VOC/Particulate Matter (PM) Speciation Database Management System (SPECIATE), the Crosswalk/Air Toxic Emission Factor Data Base Management System (XATEF), and the Test Methods Storage and Retrieval System maintained by the Emission Measurement Technical Information Center (EMTIC/TSAR). No emissions test data for the primary copper smelting industry are contained in these databases.
- 6. The EPA *Clearinghouse for Inventories and Emission Factors* (CHIEF) and *National Air Toxics Information Clearinghouse* (NATICH). No emissions test data for the primary copper smelting industry are contained in these databases.

The following general criteria were used to select pertinent references:

- 1. Emissions data must be from a primary reference; i.e., the document must constitute the original source of test data. For example, a technical paper was not included if the original study was contained in the previous document.
- 2. The referenced study must contain test results based on more than one test run.
- 3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions.

For source categories for which no primary emissions data were found and emission factors in the previous version of the corresponding AP-42 section were based entirely upon secondary data, these secondary data were again used for emission factor development. The quality of these factors was reevaluated based upon the criteria discussed below, and emission factor quality ratings were assigned accordingly. The final set of reference materials utilized in the revision of this AP-42 section is discussed in Chapter 4.0 of this background report.

3.2 Emission Data Quality Rating System

As part of the of the emissions data analysis, the quantity and quality of the information contained in the final set of reference documents were evaluated. The following data were always excluded from consideration.

- 1. Test series averages reported in units that cannot be converted to the selected reporting units;
- Test series representing incompatible test methods (e.g., comparison of the EPA Method 5 front-half with the EPA Method 5 front- and back-half);

- 3. Test series of controlled emissions for which the control device is not specified;
- 4. Test series in which the source process is not clearly identified and described; and
- 5. Test series in which it is not clear whether the emissions were measured before or after the control device.

Since no original test data were found, no test rating system was used. The rating system used by the OAQPS for the preparation of AP-42 sections is given below:

А

Multiple tests performed on the same source using sound methodology and reported in enough detail for adequate validation. These tests do not necessarily conform to the methodology specified in the EPA reference test methods, although these methods were certainly used as a guide for the methodology actually used.

B

Tests that were performed by a generally sound methodology but lack enough detail for adequate validation.

С

Tests that were based on an untested or new methodology or that lacked a significant amount of background data.

D

Tests that were based on a generally unacceptable method but may provide an order-ofmagnitude value for the source.

The following criteria is used to evaluate source test reports for sound methodology and adequate detail:

- 1. <u>Source operation</u>. The manner in which the source was operated is well documented In the report. The source was operating within typical parameters during the test.
- 2. <u>Sampling procedures</u>. The sampling procedures conformed to a generally acceptable methodology. If actual procedures deviated from accepted methods, the deviations are well documented. When this occurrs, an evaluation is made of the extent to which such alternative procedures could influence the test results.
- Sampling and process data. Adequate sampling and process data are documented in the report. Many variations can occur unnoticed and without warning during testing. Such variations can induce wide deviations in sampling results. If a large spread

between test results cannot be explained by information contained in the test report, the data are suspect and are assigned a lower rating.

4. <u>Analysis and calculations</u>. The test reports contain original raw data sheets. The nomenclature and equations used are compared to those (if any) specified by the EPA to establish equivalency. The depth of review of the calculations was dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn was based on factors such as consistency of results and completeness of other areas of the test report.

3.3 Emission Factor Quality Rating System

The quality of the emission factors developed from analysis of the test data was rated utilizing the following general criteria:

A (Excellent)

Developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

B (Above average)

Developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

C (Average)

Developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

D (Below average)

The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are noted in the emission factor table.

E (Poor)

The emission factor was developed from C- and D-rated test data, and there is reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are always noted.

The use of these criteria is somewhat subjective and depends to an extent on the individual reviewer.

3.4 References for Chapter 3.0

- <u>Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42</u> <u>Sections</u>. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Technical Support Division, Research Triangle Park, NC, 27711, April, 1992. [Note: this document is currently being revised at the time of this printing.]
- 2. <u>Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area</u> <u>Sources</u>, Supplement A, Appendix C.2, "Generalized Particle Size Distributions." U.S. Environmental Protection Agency, October 1986.

4.0 POLLUTANT EMISSION FACTOR DEVELOPMENT

4.1 Criteria Pollutant Emission Data

Particulate Matter

Due to a lack of available and recently developed emission data for the primary copper smelting industry, no revised particulate matter emission factors were developed during this update. The sources from which the emission factors presented in the previous AP-42 section are derived were reviewed, and the factors appear to have been calculated and compiled correctly, but many of these factors are not judged to accurately represent current industry operations. New Source Performance Standards promulgated January 15, 1976 limit particulate matter loading in effluent from dryers, roasters, smelting furnaces, and converters at affected facilities to 50 milligrams per dry standard cubic meter (0.022 grains per dry standard cubic foot). Much of the emission testing that forms the basis for these emission factors was performed prior to 1976. Further, limitations on some of the emission test results create doubt as to their representativeness of primary copper smelting operations as they existed at the time testing was performed. As a result, these factors have been assigned ratings of "E" due to uncertainty as to their representativeness of current industry operations.

The references cited in previous versions of AP-42 Section 12.3 as being the basis for the particulate matter emission factors presented for reverberatory furnaces were not available for review. The separate emission factors presented in previous versions of the AP-42 section for reverberatory furnaces following multiple-hearth and fluidized-bed roasters have been omitted from the revised AP-42 section because this equipment configuration is no longer commercially significant (see Section 2.2 of this background report).

The particulate matter emission factors for copper converters following reverberatory furnaces presented in previous and revised versions of AP-42 Section 12.3 are derived from seven references, four of which were not available for review. The three references cited as sources of these converter factors that were reviewed during this update (References 11, 12, and 15) do not contain emission data that are suitable for emission factor development under the guidelines established by OAQPS, and are discussed in more detail in Section 4.3 of this background report.

The particulate matter emission factors for multiple-hearth roasters presented in previous and revised versions of AP-42 Section 12.3 are derived from four references, two of which were

not available for review. References 16 and 17 are discussed in detail in Section 4.3 of this background report.

No particulate matter emission factors for fluidized-bed roasters are presented in previous versions of AP-42 Section 12.3, and a lack of available data precludes the development of emission factors for this source in the revised AP-42 section.

The particulate matter emission factors for concentrate dryers presented in previous and revised versions of AP-42 Section 12.3 are derived from References 21 and 22, neither of which contain emission data that are suitable for emission factor development under the guidelines established by OAQPS. These references are discussed in more detail in Section 4.3 of this background report.

The particulate matter emission factors for electric smelting furnaces presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 15, which does not contain emission data that are suitable for emission factor development under the guidelines established by OAQPS. This reference is discussed in more detail in Section 4.3 of this background report.

Because several cited references were not available for review, the source of the particulate matter emission factors for copper converters following electric smelting furnaces presented in previous and revised versions of AP-42 Section 12.3 could not be determined.

The particulate matter emission factors for flash furnaces presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 24, which does not contain emission data that are suitable for emission factor development under the guidelines established by OAQPS. This reference is discussed in more detail in Section 4.3 of this background report. No data are available to develop emission factors specific to Outokumpu or Inco flash smelting furnaces.

The particulate matter emission factors for slag cleaning furnaces and converters serving flash furnace smelting operations presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 22, which does not contain emission data that are suitable for emission factor development under the guidelines established by OAQPS. This reference is discussed in more detail in Section 4.3 of this background report.

The size-specific particulate matter emission factors for all primary copper smelting processes presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 25, which is discussed in detail in Section 4.3 of this background report.

The fugitive particulate matter emission factors for roaster calcine discharge presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 26, which is discussed in detail in Section 4.3 of this background report. The process rate information used to calculate the factors was taken from written correspondence from the plant superintendent at the Phelps Dodge smelter tested, which was unavailable for review as part of this update. The resulting emission factors were adjusted upward to account for an estimated 90 percent capture efficiency for the process being tested.

The fugitive particulate matter emission factors for smelting furnaces presented in previous and revised versions of AP-42 Section 12.3 are derived from a reference that was unavailable for review as part of this update. The process referred to by the term "smelting furnaces" includes matte tapping and slag skimming, but the testing from which the factors are derived was performed during matte tapping only. The process rate information used to calculate the factors was taken from written correspondence from the vice president of Phelps Dodge, which also was unavailable for review. The resulting emission factors were adjusted upward to account for an estimated 90 percent capture efficiency for the process being tested.

The fugitive particulate matter emission factors for copper converters presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 29 and 31, which are discussed in detail in Section 4.3 of this background report, and from an emission test report that was unavailable for review as part of this update. The process rate information used to calculate the factors was taken from three items of written correspondence from personnel at the three primary copper smelters examined, two of which were unavailable for review as part of this update. The resulting emission factors were adjusted upward to account for estimated capture efficiencies of 50 percent at Phelps Dodge - Ajo (Reference 28 - unavailable for review), 95 percent for ASARCo - El Paso (Reference 31), and 80 percent for ASARCo - Hayden (Reference 29).

The source of the fugitive particulate matter emission factors for anode furnaces and slag cleaning furnaces could not be determined through examination of the cited references.

Lead

Emission factors for lead from roasting, smelting, and converting operations presented in previous and revised versions of AP-42 Section 12.3 are reportedly taken from Reference 33, *Lead*

Emissions from Primary Copper Smelters. Sampling was conducted at seven primary copper smelters in the late 1970's in order to develop New Source Performance Standards (NSPS) for sulfur dioxide and National Emission Standards for Hazardous Air Pollutants (NESHAP) for arsenic emissions from these sources. Secondary laboratory analyses for lead were conducted by atomic absorption on the particulate samples collected in order to provide additional data for the use of EPA personnel. It is not apparent that the emission factors for lead presented in previous versions of AP-42 Section 12.3 are taken directly from this document, which contains tables summarizing both test-specific and aggregated emission factors for various processes. The raw data contained in the report are difficult to decipher (including the reporting units used), and do not allow the revision of existing factors. A more detailed discussion of Reference 33 appears in Section 4.3 of this background report. Based upon the uncertainties discussed in Section 4.3, these factors have been assigned a quality rating of "E."

Sulfur Dioxide

Due to a lack of available and recently developed emission data for the primary copper smelting industry, no revised sulfur dioxide emission factors were developed during this update. The sources from which the emission factors presented in the previous AP-42 section are derived were reviewed, and the factors appear to have been calculated and compiled correctly, but many of these factors are not judged to accurately represent current industry operations. New Source Performance Standards promulgated January 15, 1976 limit sulfur dioxide concentration in effluent from roasters, smelting furnaces, and converters at affected facilities to 0.065 percent by volume, or 650 parts per million by volume (ppmv). Much of the emission testing that forms the basis for these emission factors was performed prior to 1976. As a result, these factors have been assigned ratings of "E" due to uncertainty as to their representativeness of current industry operations.

The references cited in previous and revised versions of AP-42 Section 12.3 as being the basis for the sulfur dioxide emission factors presented for reverberatory furnaces were not available for review. The separate emission factors presented in previous versions of the AP-42 section for reverberatory furnaces following multiple-hearth and fluidized-bed roasters have been omitted from the revised AP-42 section because this equipment configuration is no longer commercially significant (see Section 2.2 of this background report).

The sulfur dioxide emission factors for copper converters following reverberatory furnaces presented in previous and revised versions of AP-42 Section 12.3 are derived from seven references, four of which were not available for review. The three references cited as sources of these converter factors that were reviewed during this update (References 11, 12, and 15) do not contain emission data that are suitable for emission factor development under the guidelines established by OAQPS, and are discussed in more detail in Section 4.3 of this background report.

The sulfur dioxide emission factors for multiple-hearth roasters presented in previous and revised versions of AP-42 Section 12.3 are derived from four references, two of which were not available for review. References 16 and 17 are discussed in detail in Section 4.3 of this background report.

The sulfur dioxide emission factors for fluidized-bed roasters presented in previous and revised versions of AP-42 Section 12.3 are derived from a reference that was not available for review.

The sulfur dioxide emission factors for concentrate dryers presented in previous and revised versions of AP-42 Section 12.3 are derived from References 21 and 22, neither of which contain emission data that are suitable for emission factor development under the guidelines established by OAQPS. These references are discussed in more detail in Section 4.3 of this background report.

The sulfur dioxide emission factors for electric smelting furnaces following fluidized-bed roasters presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 23, which does not contain emission data that are suitable for emission factor development under the guidelines established by OAQPS. This reference is discussed in more detail in Section 4.3 of this background report.

The sulfur dioxide emission factors for electric smelting furnaces following concentrate dryers presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 15, which does not contain emission data that are suitable for emission factor development under the guidelines established by OAQPS. This reference is discussed in more detail in Section 4.3 of this background report.

The sulfur dioxide emission factors for copper converters following electric smelting furnaces presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 15, which does not contain emission data that are suitable for emission factor

development under the guidelines established by OAQPS. This reference is discussed in more detail in Section 4.3 of this background report.

The sulfur dioxide emission factors for flash furnaces presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 24, which does not contain emission data that are suitable for emission factor development under the guidelines established by OAQPS. This reference is discussed in more detail in Section 4.3 of this background report. No data are available to develop emission factors for Outokumpu or Inco flash smelting furnaces.

The sulfur dioxide emission factors for slag cleaning furnaces and converters serving flash furnace smelting operations presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 22, which does not contain emission data that are suitable for emission factor development under the guidelines established by OAQPS. This reference is discussed in more detail in Section 4.3 of this background report.

The estimated typical sulfur dioxide concentrations in offgases from Outokumpu and Inco flash smelting furnaces presented in the revised version of AP-42 Section 12.3 are taken from a book entitled <u>Flash Smelting: Analysis, Control and Optimization</u>, which is discussed in Section 2.4 of this background report. Estimated typical sulfur dioxide concentrations for multiple-hearth and fluidized-bed roasters; reverberatory, electric, and continuous smelting furnaces; single- and double-contact sulfuric acid plants; and Pierce-Smith and Hoboken converters presented in previous and revised versions of AP-42 Section 12.3 are taken from a 1975 report entitled "Evaluation of the Controllability of SO₂ Emissions from Copper Smelters in the State of Arizona," which is discussed in Section 3.1 of this background report.

The fugitive sulfur dioxide emission factors for roaster calcine discharge presented in previous and revised versions of AP-42 Section 12.3 are derived from References 16 and 26, which are discussed in detail in Section 4.3 of this background report. The process rate information used to calculate the factors was taken from written correspondence from personnel at the two primary copper smelters examined, both of which were unavailable for review as part of this update. The resulting emission factors were adjusted upward to account for an estimated 90 percent capture efficiency at each of the two smelters.

The fugitive sulfur dioxide emission factors for smelting furnaces presented in previous and revised versions of AP-42 Section 12.3 include matte tapping and slag skimming operations. These factors are derived from emission testing on both types of operations at ASARCo - Tacoma

(Reference 16) and Kennecott - Magna (Reference 27), and on matte tapping operations at Phelps Dodge - Ajo (Reference 28 - unavailable for review). The process rate information used to calculate the factors was taken from three items of written correspondence from personnel at these three smelters, all of which were unavailable for review. The resulting emission factors were adjusted upward to account for estimated capture efficiencies of 90 percent in all cases.

The fugitive sulfur dioxide emission factors for copper converters presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 29, which is discussed in detail in Section 4.3 of this background report, and from two emission test reports that were unavailable for review as part of this update. The process rate information used to calculate the factors was taken from three items of written correspondence from personnel at the three primary copper smelters examined, all of which were unavailable for review as part of this update. The resulting emission factors were adjusted upward to account for estimated capture efficiencies of 50 percent at Phelps Dodge - Ajo (Reference 28 - unavailable for review) and Phelps Dodge - Playas (Reference 30 - unavailable for review), and 80 percent at ASARCo - Hayden (Reference 29).

The fugitive sulfur dioxide emission factors for converter slag return presented in previous and revised versions of AP-42 Section 12.3 are derived from Reference 16, which is discussed in detail in Section 4.3 of this background report. The process rate information used to calculate the factors was taken from written correspondence from the plant manager of the ASARCo - Tacoma primary copper smelter, which was unavailable for review as part of this update. The resulting emission factors were adjusted upward to account for an estimated 90 percent capture efficiency at the process tested.

The source of the fugitive sulfur dioxide emission factors for anode furnaces and slag cleaning furnaces could not be determined through examination of the cited references.

Nonmethane Organic Compounds.

Due to a lack of data quantifying emissions of organic compounds from processes associated with the primary copper smelting industry, no emission factors for these pollutants are presented in either the previous or revised versions of AP-42 Section 12.3.

Nitrogen Oxides.

No data on emissions of oxides of nitrogen were found directly from processes associated with the secondary copper processing industry. It can be assumed that these compounds are emitted from in-process heating units, but no quantitative data are available.

Carbon Monoxide.

No data on emissions of carbon monoxide were found directly from processes associated with the secondary copper processing industry. It can be assumed that this compound is emitted from in-process heating units, but no quantitative data are available.

4.2 Noncriteria Pollutant Emissions Data

Hazardous Air Pollutants.

Among the compounds defined in the 1990 Clean Air Act Amendments as Hazardous Air Pollutants (HAP's) are compounds of arsenic, antimony, lead, and nickel. All of these compounds, especially oxides and sulfides of these metals, are emitted from primary copper smelting operations in quantities that vary with their content in the ore used as raw material. No quantitative emissions data suitable for use in emission factor development are available for any HAP's other than lead, which is discussed in Section 4.1 of this background report.

Several of the emission tests utilized in the development of emission factors presented in previous and revised versions of AP-42 Section 12.3 include arsenic emission data. However, these data are not felt to accurately represent current operations at domestic primary copper smelters. A "National Emission Standard for Inorganic Arsenic Emissions from Primary Copper Smelters" (NESHAP) was promulgated in August 1986, and all of the available emission test data results from testing performed before that date.

Global Warming Gases.

Pollutants such as methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O) have been found to contribute to overall global warming. No data on emissions of these pollutants were found for the primary copper smelting processes. The prevalence of pyrometallurgical processes makes the likelihood of carbon dioxide emissions high, but data to quantify these emissions are not available.

Stratospheric Ozone-Depleting Gases.

Gases such as chloroflourocarbons, hydrochloroflourocarbons, carbon tetrachloride, methyl chloroform, and halons have been found to contribute to depletion of the stratospheric ozone layer. No data suggesting the existence of any of these pollutants in emissions from primary copper smelting processes were expected nor found.

4.3 Review of Specific Data Sets

<u>Reference 11:</u> <u>Measurement of Sulfur Dioxide, Particulate, and Trace Elements in Copper</u> <u>Smelter Converter and Roaster/Reverberatory Gas Streams</u>

This document details the results of emission testing performed by the EPA in September 1973 on the ASARCo primary copper smelter in Tacoma, Washington. Testing was performed for SO_2 , particulate matter (including particle sizing), arsenic, cadmium, chromium, copper, lead, and zinc. Test procedures are well documented, but no field nor analytical data are included in the report. No process rate information is contained in this report, precluding its use in developing emission factors. The particle size distributions presented in this document for ESP-controlled and uncontrolled emissions from the converter and the combined vent serving the multiple-hearth roaster and reverberatory furnace are the basis for the size-specific particulate matter emission factors from these sources presented in the revised AP-42 Section 12.3 (see Reference 25 below).

Reference 12: Handwritten Notes

This one-page, handwritten table is titled "Reverb & Roaster Stack Emission," and probably pertains to the ASARCo primary copper smelter in Tacoma, Washington. Columns of data for emissions, roaster feed, feed percent copper, converter feed, and blister percent copper are presented on a monthly basis for 1967 - 1972. These data are not suitable for use in emission factor development.

Reference 15: "Inspiration's Design for Clean Air"

This article from the June 1974 edition of *Engineering and Mining Journal* examines the recent installation of an electric smelter and a double-contact sulfuric acid plant at the Inspiration Consolidated Copper Co. facility in Arizona. This expenditure was made primarily in response to the EPA's newly promulgated regulations. This article provides general information on capacity

and typical operating parameters, but does not contain any data suitable for emission factor development.

References 16-17: *Emission Test Report - ASARCo, Tacoma, WA, September 1978* and associated operational data

The emission factor for sulfur dioxide from multiple hearth roasting presented in previous versions of AP-42 Section 12.3 is derived in some fashion from the results of the emission testing documented in this report. This smelter, which is no longer in operation, processed ores of unusually high arsenic content (0.7 to 0.9 percent by weight). A series of emission tests was performed as part of the development of New Source Performance Standards (NSPS) for sulfur dioxide and the NESHAP for arsenic from primary copper smelters. The sample collection and analysis methodologies utilized in performing these tests are well documented and appear to be technically sound.

Included among these tests were three runs each at the inlet and outlet of the baghouse serving a multiple hearth roaster. The charge to the roaster on the day during which the first two runs were conducted was 1135 tons, and on the day of the third run was 1163 tons. Sulfur dioxide emission rates for the three runs at the baghouse inlet, measured by a method similar to EPA Reference Method 8, were reported as being 11,331.6837; 16,776.0859; and 14,908.5969 pounds per hour, respectively. The accuracy of these values is not felt to warrant the reporting of nine significant figures. The emission factor indicated by these values is approximately 300 pounds per ton of charge. The emission factor reported in the previous version of AP-42 Section 12.3 is 280 pounds per ton, with no documentation of how this value was calculated.

Reference 21: Compliance Status Memorandum, Inspiration Consolidated Copper Co.

This memorandum, which gives no indication as to its date, originator, or intended audience, summarizes the compliance status of the Inspiration smelter in Arizona throughout the 1970's. No data suitable for use in emission factor development are contained in this reference.

Reference 22: Written Communication from Phelps Dodge to EPA

This memorandum to the director of the Emission Standards and Engineering Division includes a process flow chart and a number of tables presenting various operational data and control equipment parameters for the Phelps Dodge primary copper smelter in Douglas, Arizona. No data suitable for use in emission factor development are contained in this reference.

Reference 23: Written Communication from Anaconda to EPA

This memorandum to the director of the Emission Standards and Engineering Division includes as attachments a number of equipment configurations and tables presenting various operational data for the Anaconda primary copper smelter in Anaconda, Montana. No data suitable for use in emission factor development are contained in this reference.

Reference 24: Telecon with Phelps Dodge

This 1982 telephone conversation report summarizes information received in the course of developing New Source Performance Standards for primary copper smelters. The Phelps Dodge personnel estimated that:

- 1) SO_2 content in the gas exiting the waste heat boiler is 9.5 percent;
- 2) 14 percent of the furnace charge is emitted as particulate matter; and
- 3) half of this particulate matter settles in the waste heat boiler, and the remaining half is collected in the ESP.

No data suitable for use in emission factor development are contained in this reference.

Reference 25: Nonferrous Industry Particulate Emissions: Source Category Report

This comprehensive 1986 study includes a review of much of the data utilized in development of previous versions of AP-42 Section 12.3. In particular, all particle size distribution information contained in these previous versions was compiled for, and first presented in, this document.

Size-specific particulate matter emission factors for fugitive emissions from reverberatory furnace matte tapping operations and from reverberatory furnace slag tapping operations presented in this reference and in previous and revised versions of AP-42 Section 12.3 are reportedly derived from a series of tests performed at the Kennecott - Hayden primary copper smelter. Several of the test runs utilized for development of emission factors had isokinetic sampling ratios of less than 90 percent, indicating that the results from these runs may not be representative.

The particle size distribution for fugitive emissions from converter slag and copper blow operations presented in this reference and in previous and revised versions of AP-42 Section 12.3 is

reportedly derived from a series of tests performed at the Phelps Dodge - Playas primary copper smelter. The report detailing this series of tests contains minimal documentation of sampling conditions, and no process data are reported. Reference 25 provides no explanation of the emission factors to which this particle size distribution was applied to arrive at the size-specific particulate matter emission factors presented.

The particle size distributions used to develop the size-specific particulate matter emission factors for a multiple hearth roaster and reverberatory smelting furnace (vented to the same inseries ESP's) and for copper converter operations presented in this reference and in previous and revised versions of AP-42 Section 12.3 are taken from Reference 11, <u>Measurement of Sulfur</u> <u>Dioxide, Particulate, and Trace Elements in Copper Smelter Converter and Roaster/Reverberatory</u> <u>Gas Streams</u>. As discussed above, Reference 11 provides no process data. In addition, the particle size distributions presented in Reference 11 are afforded little confidence by the sampling team reporting the data, because the control devices are shown to exhibit negative control efficiencies in several size ranges. No explanation is provided in Reference 25 as to the particulate matter emission factors to which these questionable particle size distributions was applied to arrive at the size-specific emission factors presented.

The particle size distribution for emissions from reverberatory smelter operations presented in this reference and in previous and revised versions of AP-42 Section 12.3 is reportedly derived from a series of tests performed at the Phelps Dodge - Ajo primary copper smelter. The report detailing this series of tests contains no documentation of sampling conditions. Reference 25 provides no explanation of the emission factors to which this particle size distribution was applied to arrive at the size-specific particulate matter emission factors presented.

Reference 26: Emission Test Report - Phelps Dodge, Douglas, AZ, May 1978

This report details the results of emission testing performed at the inlet and outlet of a baghouse serving a railcar loading operation. This is an intermittent process, in which calcine from the roaster is transferred to railcars. Testing for arsenic and sulfur dioxide was performed in order to develop NSPS for primary copper smelters, and particulate emissions were also quantified, including a particle size distribution analysis. Testing at the inlet and outlet were not performed simultaneously, precluding the calculation of control equipment efficiency. No process data are

included in the report, precluding the calculation of test-specific emission factors for any pollutants.

Reference 27: Emission Test Report - Kennecott, Magna, UT, October/November 1978

This report details the results of emission testing performed in order to quantify fugitive emissions of arsenic and sulfur dioxide from matte and slag tapping operations and a converter and non-fugitive emissions from a rotary concentrate dryer and a converter. These tests were performed in order to develop NSPS for primary copper smelters. Testing in the converter fugitive collection system duct and at the inlet to the sulfuric acid plant to which the converter hood is ducted was not performed simultaneously, precluding a determination as to the capture efficiency of the converter hood. No process data are included in the report, precluding the calculation of test-specific emission factors for any pollutants.

Reference 29: ASARCo Correspondence, May 1980

The attachment to this reference briefly summarizes the results of emission testing performed by ASARCO engineers on the secondary converter flue system at an unspecified copper smelter. Emissions of oxides of sulfur and particulate matter, including analyses for arsenic, copper, lead, silver, and zinc were quantified. Sample collection and analysis procedures are reasonably well documented in this attachment and are supported by field and lab data, but isokinetic sampling ratios were as low as 85 percent, and no estimation of process rates during testing are provided.

Reference 31: Emission Test Report - ASARCo, El Paso, TX, January 1978

This report details the results of testing performed in order to quantify emissions of particulate matter, sulfur dioxide, and arsenic from a calcine loading operation, a matte tapping operation, a gas cleaning system serving a roaster and a reverberatory furnace, and fugitive emissions from the converter building. Testing for arsenic and sulfur dioxide was performed in order to develop NSPS for primary copper smelters. Sample collection and analysis procedures are reasonably well documented in this attachment and are supported by field and lab data, but no estimation of process rates during testing are provided, precluding the calculation of test-specific emission factors for any pollutants.

Reference 32: "Measurement of Fugitive Particulate and Sulfur Dioxide Emissions at Inco's Copper Cliff Smelter"

This technical paper details the results of extensive research done by Inco engineers to quantify fugitive emissions from what was, at the time of testing, the world's largest nonferrous smelting facility. The data in this paper are not useful for the development of emission factors because all testing was performed in one of 44 ventilation ducts serving the same facility over an extended period of time. When tested, this facility produced both nickel and copper, and contained six reverberatory furnaces, one flash furnace, and nineteen converters. The only documentation of operational conditions is that they were "normal."

Reference 33: Lead Emissions from Primary Copper Smelters

Emission factors for lead from roasting, smelting, and converting operations presented in previous versions of AP-42 Section 12.3 are reportedly taken from this document. Sampling was conducted at seven primary copper smelters in the late 1970's in order to develop NSPS for sulfur dioxide and NESHAP for arsenic emissions from these sources. Secondary laboratory analyses for lead were conducted by atomic absorption on the particulate samples collected in order to provide additional data for the use of EPA personnel. Reports detailing the primary results of four of these seven emission test series are reviewed above, as References 16, 26, 27, and 31.

It is not apparent that the emission factors for lead presented in AP-42 Section 12.3 are taken directly from this document, which contains tables summarizing both test-specific and aggregated emission factors for various processes. The raw data contained in the report are difficult to decipher (including the reporting units used). This emission data set has thus been assigned a quality rating of "D."

4.4 Data Gap Analysis

A significant data gap exists for emissions of all pollutants from the primary copper smelting industry, insofar as current data were unavailable for the development of emission factors. Given that this industry is comprised of only eight facilities, and that these facilities utilize five different types of processes (soon to be six - see Section 2.2 of this background report), it is reasonable to assert that quantification of emissions from this industry is justifiable. The factors do not reflect the fact that several of these plants have made significant modifications, including the installation of efficient on-site sulfuric acid plants and new smelting furnaces utilizing flash smelting technology, since the promulgation of New Source Performance Standards in 1976.

4.5 References for Chapter 4.0

- 1. J.L.W. Jolly, "Copper," <u>Mineral Commodity Summaries 1992</u>, U.S. Department of the Interior, Bureau of Mines, Washington, DC, 1992.
- 2. J.L.W. Jolly, "Copper," <u>Minerals Yearbook 1989</u>, U.S. Department of the Interior, Bureau of Mines, Washington, DC, 1990.
- 3. <u>Background Information Document for Revision of New Source Performance Standards for</u> <u>Primary Copper Smelters</u>, EPA Contract No. 68-02-3056, Research Triangle Institute, Research Triangle Park, NC March 31, 1982.
- 4. <u>Air Pollution Emission Test: Asarco Copper Smelter, El Paso, TX</u>, EMB-77-CUS-6, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1977.
- 5. Written Communication from W.F. Cummins, Inc., El Paso, TX, to A.E. Vervaert, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1977.
- 6. AP-42 Background Files, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1978.
- Source Emissions Survey of Kennecott Copper Corporation, Copper Smelter Converter Stack Inlet and Outlet and Reverberatory Electrostatic Precipitator Inlet and Outlet, Hurley, NM, Ecology Audits, Inc., Dallas, TX, April 1973.
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TABLE 4.5-1

LIST OF CONVERSION FACTORS

Multiply:	by:	To obtain:
mg/dscm	4.37 x 10 ⁻⁴	gr/dscf
m ²	10.764	ft ²
m ³	35.31	ft ³
m	3.281	ft
kg	2.205	lb
kPa	0.145	psia
kg/Mg	2.0	lb/ton
Mg	1.1023	ton

Temperature conversion equations:

Fahrenheit to Celsius:

$$^{\circ}C = \frac{(^{\circ}F - 32)}{1.8}$$

Celsius to Fahrenheit:

 $^{\circ}F = 1.8(^{\circ}C) + 32$