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EMISSION FACTORS AND EMISSION SOURCE INFORMATION FOR PRIMARY AND SECONDARY COPPER SMELTERS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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EMISSION FACTORS AND EMISSION SOURCE INFORMATION FOR PRIMARY AND SECONDARY COPPER SMELTERS

by

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Contract No. 68-02-1890
Task Order No. 3

EPA Project Officer: Arch McQueen

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
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ABSTRACT

This document constitutes the final report of a project, carried out under U.S. EPA Contract No. 68-02-1890 (Task Order No. 3), to upgrade emission factors and engineering management information for primary and secondary copper smelters. The main body of the report describes procedures and methodology used in obtaining relevant information regarding these industries and the operational characteristics of process equipment used therein. Related information regarding alloying and casting has been included in the description secondary copper smelter processes, and information about emissions from similar furnaces used in nonferrous foundry operations was also collected. New information on source tests was coded for entry into the AEROS SOTDAT files; newly identified sources were coded for entry into NEDS, and information as to the precision of emission factors was furnished for use in the SIEFA data base. New source classification codes (SCC's) were proposed for a number of processes.

Appendixes to this document are the following project deliverables: Appendixes A and B for inclusion in AP-42, "Compilation of Air Pollutant Emission Factors," namely Section 7.3, Primary Copper Smelting and Section 7.9, Secondary Copper Smelting and Alloying; Appendix C, Primary Copper Smelting Process Compendium; and Appendix D, Secondary Copper Smelting Process Compendium.

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1.0 INTRODUCTION

This report describes the methodology followed and the results achieved by Pacific Environmental Services, Inc. (PES) pursuant to EPA Contract No. 68-02-1890, Task Order No. 3, initiated in October 1976.

1.1 SCOPE OF WORK

The scope of work for this project called for an intensive engineering evaluation of air pollutant emission sources at primary and secondary copper smelters in the United States. It required collection of reference data for primary smelters and for the secondary smelting and alloying industry, as well as the development of emission factors for major types of air-pollution emitting operations and equipment.

1.2 TASK DESCRIPTION

Deliverables contemplated by the contract included a series of documents dealing with process descriptions and emission factors for primary and secondary copper smelter emission sources. These documents were to be prepared in formats consistent with those of the following publications:

1. AP-42, "Compilation of Air Pollutant Emission Factors"*
2. "Engineering Support Manual for NEDS Users"(Ref. 2)
3. AP-42, Appendix C, Source Classification Codes

In addition, machine-readable data inputs were required for updating AEROS component data systems: SOTDAT, NEDS, and SIEFA.

Subtasks designed for the implementation of the work were as follows:

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* Reference 1, hereafter referred to as "AP-42."

1. Preparation of a list of information sources, including governmental agencies, research organizations, consultants, and nonferrous smelter industry experts, and preparation of a bibliography.
2. Contacting the information sources to obtain information on process descriptions for both primary and secondary smelters and documented point source emissions data both for criteria pollutants and for certain other non-criteria pollutants, including arsenic, cadmium, lead, beryllium, boron, and antimony. The best available information on fugitive emissions was also to be obtained.
3. Analysis of the data to determine emission factors and the AEROS systems input elements.

1.3 ORGANIZATION OF FINAL REPORT

The remainder of this report consists of five sections (Sections 2.0 to 6.0). In Section 2.0, results and conclusions emerging from the study are briefly summarized. In Section 3.0, experience gained in carrying out the data-gathering task is recounted and discussed. In Section 4.0, the methodology of data analysis is reviewed and the results summarized and discussed, in terms of emission factors developed for both primary and secondary smelters. Section 5.0 reviews findings related to the nature and sources of fugitive emissions in smelter operations and discusses suggested means of control or abatement of these emissions. Finally, recommendations regarding further source testing to improve knowledge of smelter emissions, emission factors, and the conditions affecting them are presented and discussed in Section 6.0.

2.0 RESULTS AND CONCLUSIONS

This section summarizes the results obtained and conclusions derived from the study of primary and secondary copper smelting operations.

2.1 PROJECT DELIVERABLES

Products delivered to the Project Officer, in addition to this report and monthly progress reports, include:

1. Process Compendiums for primary and secondary copper smelters.
2. Sections for AP-42, "Compilation of Air Pollutants Emission Factors," for primary and secondary copper smelters.
3. Coding forms for information for AEROS component systems SOTDAT and NEDS, regarding primary and secondary copper smelters. (Since coding forms for SIEFA information have not been designed, SIEFA information is provided only in this report, Section 6.1).

2.2 DEVELOPMENT OF EMISSION FACTORS

The primary objective of this project was to develop new or modified emission factors for particulates from primary and secondary copper smelters and for sulfur dioxide from primary copper smelters. The target approach was to obtain up-to-date reliable emissions test data from as many sources as possible, to arrange these data into logical form, and to calculate both uncontrolled and controlled emission factors for as many source categories as seemed reasonable.

In the case of secondary copper smelting (sometimes called refining), a single furnace operation is almost always involved. Several types of furnaces are utilized in this industry, and emission factors were developed for each of the five types covered in this study. Table 2-1 shows both the emission factors for particulates

Table 2-1. EMISSION FACTORS FOR PARTICULATES FROM SECONDARY COPPER SMELTING AND ALLOYING PROCESSES WITHOUT CONTROLS, COMPARED WITH PUBLISHED FACTORS (AP-42, BRASS AND BRONZE MELTING FURNACES)*

Type of Furnace	kg/MT		lb/ton	
	AP-42	This Study	AP-42	This Study
Crucible	6	11	12	21
Cupola	37	0.002-120	73	0.003-240
Electric Induction	1	3.5 -10	2	7-20
Reverberatory	35	3-18	70	5-36
Rotary	30	5-150	60	10-300

*The ranges represent variations due to charge material. Average factors for these differing materials are given in Section 4.0.

as developed in this project and those currently given in AP-42. Individual test results for each type of furnace covered a fairly wide range as shown in greater detail in Section 4.2 of this report. Some of the factors contributing to this variation include (1) composition of charge: presence of volatile constituents such as arsenic, beryllium, cadmium, and zinc can substantially increase metal oxide emissions; (2) condition of charge: insulation, oil and grease can increase carbonaceous particulates; (3) heating rate: high heat input can increase emissions. Therefore, emission factors should be used with care and augmented with specific information when available.

In the case of sulfur dioxide emissions from primary copper smelters, PES feels that an approach should be taken on emission factors which differs somewhat from that now used. Some of the factors underlying that judgment are listed below:

- AP-42 currently gives factors for roasting, smelting, and converting. These factors cannot be representative for all smelters because emissions depend on sulfur content of the concentrate, and because not all smelters are configured similarly.
- Source tests at some smelters have not dealt with individual sources but with combined effluents from two or more processing units.
- Even for a single point source, test results are not necessarily representative because they depend on the current value of the variable sulfur content of concentrate.
- We have not found any measurements to indicate the actual magnitude of sulfur loss by fugitive emissions.
- Smelting plants without roasters would naturally be expected to have higher emission factors for their other processing units because more sulfur must be removed in these other units.

Consequently, in this study uncontrolled SO_2 emission factors for primary copper smelters have been prepared using the following assumptions:

1. Sulfur content of the concentrate is 32 percent (the national average; varies from a low of 8 percent to a high of 38 percent).
2. Two configurations of smelters are considered - the first including roasting, reverberatory smelting, and converting; the second including only reverberatory smelting and converting.
3. Sulfur dioxide emissions are allocated among the various point sources plus fugitive emissions and slag according to the figures given in the EPA NSPS Background Document for Primary Copper Smelters, EPA 450/2-74-002a. (Ref. 3)

Based upon these assumptions, which are reasonably consistent with source test data obtained in this study, uncontrolled SO_2 emission factors for primary copper smelting are given in Table 2-2 and compared with those currently given by AP-42. There are more individual factors recommended than are presently given by AP-42 and there are some differences in factors for individual processes, but the total uncontrolled SO_2 emissions per ton of concentrate processed remains almost the same.

Factors for controlled sulfur dioxide emissions depend strongly upon the type of control and the portion of the entire smelting operation served by the controls. While there are few smelters with controls on low concentration SO_2 gas streams such as from multiple-hearth roasters and reverberatory smelting furnaces, this situation is changing. Also, some smelters have controls on only a portion of the emissions from any given process. Finally, the increasing use of double contact sulfuric acid plants as control systems has increased control efficiency in some cases from 95 percent for single contact plants to 98 or 99 percent for the double contact plants.

In the case of uncontrolled particulate emissions from primary copper smelters, there is no method of estimating emissions except through the use of source test data. Because of the variability in facilities, operating conditions, feed materials, and test

Table 2-2. EMISSION FACTORS FOR SULFUR DIOXIDE FOR PRIMARY COPPER SMELTING PROCESSES WITHOUT CONTROLS

Configuration No. 1

Process	SO_2 Emissions, kg/MT (lb/ton) Concentrate	
	Recommended	Current AP-42*
Roasting	205 (410)	30 (60)
Reverberatory Furnace	115 (230)	160 (320)
Converting	270 (540)	435 (870)
Fugitive Emissions	37 (74)	-
Total Uncontrolled	627 (1,254)	625 (1,250)

Configuration No. 2

Reverberatory	195 (390)	-
Converting	430 (860)	-
Fugitive Emissions	2 (4)	-
Total Uncontrolled	627 (1,254)	-

*In the current AP-42 only one set of emission factors are given. No distinction is made as to smelter configuration.

methods, it is likely that results from one group of tests will differ from those obtained from another group unless both groups are very large and unbiased in the parameters influencing the results. Therefore, the results of this study were used to modify the current AP-42 emission factors on the assumption that increasing the test base decreases the standard error.

No additional information was obtained on uncontrolled particulates from roasting or fire refining nor was information obtained on potential additional sources of particulates not currently covered in AP-42, such as concentrate and flux crushers anode furnaces, and newer smelting processes - electric arc smelting and flash smelting. Uncontrolled particulate emission factors developed from this study are compared with those currently given in AP-42, and recommended new factors are given in Table 2-3.

Controlled particulate emissions depend strongly upon the type and capacity of control equipment. Electrostatic precipitators are widely used in the primary copper smelting industry. High efficiency scrubbers are used as supplementary control in many cases where additional particulate control is required prior to feeding exhaust gases to sulfuric acid plants. Efficiencies from 95 percent to 99 percent can be attained.

Much additional information on emissions of SO_2 and particulates from both primary and secondary copper smelting is given in Section 4.0 of this report. Tables summarizing the data provide information on the range of results obtained and the number of tests available. Fugitive emissions are discussed in Section 5.0.

Precisions of the emission factors developed in this study and the need for additional source tests are discussed in Section 6.0. For primary smelting processes the precision (standard error) of the factors is generally less than 35 percent for

Table 2-3. EMISSION FACTORS FOR PARTICULATES FROM PRIMARY COPPER SMELTING PROCESSES WITHOUT EMISSION CONTROLS

Process	Particulate Emissions, kg/MT (lb/ton) Concentrate		
	This Study	Current AP-42	Recommended
Roasting	-	22.5 (45)	22.5 (45)
Reverberatory Smelting	26 (52)	10 (20)	18 (36)
Converting	12 (24)	30 (60)	21 (42)
Refining	-	5 (10)	5 (10)
Total Uncontrolled	-	67.5 (135)	66.5 (133)

particulates and ranges between 9 and 78 percent. Substantial additional testing on individual processes and on sources not heretofore considered is recommended.

3.0 DATA GATHERING

The data gathering task for this project was performed in order to establish a documented base for the development of emission factors for copper smelting emission points. The task was twofold in the sense that project engineers were required to obtain data from all available information sources, and also were to identify areas where current data were nonexistent. This meant that for some emission points, the effort would have to be exhaustive, to insure that all reasonable sources of information had been investigated.

The principal objective of this task, therefore, was to gather emission-related data in the form of source test reports, emission inventory reports, material balances, etc. Another requirement of the project was that the process-related information obtained be prepared in the form of process compendiums for the primary and secondary copper smelting industries. Data necessary for these reports would include process flow sheets, equipment operating parameters, and raw material and product compositions.

Initially, project personnel established five areas to be investigated for possible contributions in the data gathering phase. These were (1) PES in-house files for 13 of the 15 primary copper smelters, (2) trade literature, (3) professional organizations, (4) governmental agencies, and (5) the smelters themselves. Other sources such as control equipment manufacturers were also considered; however, it was thought that the five identified categories would provide the bulk of the data for the project. In support of the five information areas, project engineers prepared an initial "Resource Information List" which contained names of individuals and organizations which would be contacted for possible information. The list was discussed with the Project Officer and was augmented at the time

to include a particular individual in each of the 10 EPA regional offices who would be the initial contact for the data gathering effort in that regi. . In many cases, this individual was the person who had responsibility for the region's NEDS data system. In some regions, however, PES personnel had worked with a particular person on a previous copper smelter project who had a current understanding of the region's available smelter data. All of the 10 EPA regional offices were contacted by mail and by phone as the first step in the process of obtaining data.

To reduce the amount of duplicated effort required for this task, project engineers analyzed the information which was already available in in-house files for 13 of the 15 primary copper smelters. These data had been collected in support of six previous projects which PES had performed or was performing for EPA. In previous work, a large percentage of the tasks had been spent in characterizing the operations of reverberatory furnaces in particular. Thus, it was found that a great deal of process data were available for primary smelting sources. Also, rather extensive bibliographic compilations had been made for these projects which assisted project engineers in their current literature search. Emission estimates were, in general, based upon yearly or monthly average material balances, but in some cases, source test reports were also included in the files.

Almost concurrently, project engineers began investigating technical literature on the smelting processes (Refs. 4 through 17). The EPA library was consulted for reference documents on the subjects, and technical journals were accessed at a nearby university library. Some articles were found in the Journal of Metals, Mining Engineering, and the Engineering and Mining Journal, and a number of government publications were made available through the EPA library. The Air Pollution Technical Information Center (APTIC) was called and a

list of abstracts of publications related to copper smelting was requested. The abstracts were not received, however. Little information in the technical literature contained hard emission data, but many of the documents were filled with much valuable process information. Particularly useful were documents which addressed new areas of process and control technology.

After reviewing literature sources, project engineers were able to compile a list of professional organizations which could be written to for data. The list included the following organizations:

American Bureau of Metal Statistics, New York, New York

American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, New York

American Mining Congress, Washington, D.C.

Brass and Bronze Ingot Institute, Chicago, Illinois

Cast Metal Federation, Rocky River, Ohio

Colorado Mining Association, Denver, Colorado

National Association of Recycling Industries (previously the National Association of Secondary Material Industries), New York, New York

Non-Ferrous Foundry Society, Cleveland, Ohio

Smelter Control Research Association, Columbus, Ohio

Letters were written to each of these organizations in the hope that they had conducted source testing at copper smelters for research purposes. It was known at the time that the Smelter Control Research Association (SCRA), for example, had been conducting pilot plant studies of various air pollution control devices on primary smelting processes. However, the responses from the professional organizations did not supply any hard emission data. The effort expended in contacting these sources was beneficial to staff in that some of the organizations were helpful in suggesting which people to contact at the smelter companies.

The remainder of the effort for data gathering was concentrated on governmental agencies and direct contact with the plants. In order to best access governmental file data, it was necessary to compile a list of all of the primary and secondary copper smelters in the country. The listing of primary smelters was a simple task since there are only 15 plants which are operated in the United States. To compile the listing of secondary plants, project engineers began with a plant name listing from the NEDS data base which was keyed on the SIC codes of 3341, 3351, 3362, 3432, 3446, and 3497. Only the 3341 code pertains uniquely to secondary smelters; however, it was felt that other plants whose main function might be, for instance, as a brass or bronze foundry (3362), could also maintain operations and process equipment which could be found at secondary smelters. To augment the list of sources from NEDS, a recently published report by the Radian Corporation was used. The report presented a multimedia environmental assessment of the secondary metals industry and included a company directly as an appendix. From the data presented in NEDS and the Radian report, lists were prepared of primary and secondary smelters in each of the 10 EPA regions.

Having tabulated the smelters by region, project engineers initiated contacts by letter and by telephone with govenmental agency personnel to ascertain whether relevant data might be available. Federal-, state-, and local-level agencies responded to the data requests by either sending available source test and process information or by indicating that data were available in their fields and project engineers could access the data in their offices. Based upon an evaluation of the number of possible sources in an area and the probable quantity and quality of data to be obtained, the following governmental agency offices were visited by PES personnel:

EPA, Region III, Philadelphia, Pennsylvania

Philadelphia Air Management Services, Philadelphia, Pennsylvania

New Jersey Department of Environmental Protection, Trenton, New Jersey

New Jersey Department of Environmental Protection, Metro field office, Springfield, New Jersey

New Jersey Department of Environmental Protection, Newark field office, Newark, New Jersey

New York State Department of Environmental Conservation, New York, New York

The City of New York Department of Air Resources, New York, New York

EPA, Region V, Chicago, Illinois

Cook County Department of Environmental Control, Maywood, Illinois

Wayne County Department of Health, Air Pollution Control Division, Detroit, Michigan

City of Cleveland Department of Public Health and Welfare, Division of Air Pollution Control, Cleveland, Ohio

State of Ohio Environmental Protection Agency, Columbus, Ohio

City of Chicago Department of Environmental Control, Chicago, Illinois

EPA, Region IX, San Francisco, California

Arizona Department of Health Services, Phoenix, Arizona

South Coast Air Quality Management District, Los Angeles, California

Other agencies which provided information by mail were:

EPA, National Enforcement Investigations Center, Denver, Colorado

EPA, Region IV, Atlanta, Georgia

EPA, Region VII, Kansas City, Missouri

Texas Air Control Board, Austin, Texas

Tennessee Department of Public Health, Division of Air Pollution Control, Nashville, Tennessee

Montana State Department of Health and Environmental Sciences, Helena, Montana

Puget Sound Air Pollution Control District, Seattle, Washington

Bay Area Air Pollution Control District, San Francisco, California

New Mexico Environmental Improvement Agency, Santa Fe, New Mexico

In some cases, the types of data items which were being requested from these agencies were considered to be potentially confidential in nature, and the agencies were reluctant to release the data to a private consultant. In particular, this problem was encountered in EPA, Region IX offices and in the South Coast Air Quality Management District (SCAQMD). Since these two sources were expected to be able to provide a great deal of source test data, special provisions had to be arranged to obtain the information. After many discussions with the SCAQMD, a rather simple solution to the problem was agreed upon. The SCAQMD provided copies of the complete test reports for secondary copper smelters in their jurisdiction, but company names and addresses were deleted in all tests. Eight tests were made available from this source.

The data availability problem in EPA, Region IX, required a great deal more time and effort than was initially expected, but the efforts were rewarded by the acquisition of a large number of pertinent source tests. A request for data was first made to Region IX in early February 1977. PES personnel were informed, at that time, that EPA had done testing at several of the primary smelters in Arizona, but due to impending court decisions, the tests were not immediately available. On March 8, 1977, project engineers visited EPA offices in San Francisco to again discuss the acquisition of the test data. At that time, however, it was decided that a modification to the contract would be necessary to allow PES to access potentially confidential material. Upon

approval of the Project Officer, and in accordance with the specifications set forth by Region IX, the PES contract was suitably modified, and the test results were received on April 29, 1977.

It was apparent at this point in the data gathering task that a great deal of source test data were not going to be available through governmental agencies. It was also apparent most of the testing which had been done by the agencies was performed for compliance determination purposes. As such, most of the emission measurements were taken downstream of control equipment and were often measured in gas streams which had been combined from a number of processes. Project engineers contacted other governmental agencies which were thought to be more inclined to do research testing rather than compliance testing, such as the U.S. Bureau of Mines OAQPS, and the Industrial Environmental Research Laboratory of EPA. No usable test data were obtained from these sources, however.

After making contact with 37 governmental agencies, in all, project personnel began concentrating their final efforts of this task on the smelting plants themselves. Initially, plant managers at a few of the primary smelters were written to and called. As a standard company policy, however, the plant managers referred our requests, in all cases, to central company offices. PES then contacted personnel who were in charge of environmental matters for an entire copper company. In general, the position that was taken by the copper companies was that all testing which had been performed had already been submitted to the proper governmental agency and would have to be obtained through their offices. It is not known how much of the test data presumably submitted by the smelters ultimately was obtained from the governmental agencies contacted.

4.0 DATA ANALYSIS

4.1 DATA ANALYSIS PROCEDURES

In order to facilitate the review of the data which had been gathered, a filing system was organized to allow ready access to individual items of information. Preparation of the project deliverables basically required a progression of four steps as outlined below:

1. Identification of processes
2. Writing of process descriptions
3. Analysis of source tests
4. Development of emission factors

With this framework in mind, project engineers classified the data into a series of process files. From the process file system, project personnel could withdraw data to be used in the writing of a process description or the development of an emission factor for a particular smelting process. These files ultimately were destined to serve as backup data for NADB.

The identification of processes to be included for study in this project was straightforward. The previously referenced multimedia assessment report by Radian (Ref. 18) listed the significant air pollution sources at secondary smelters. Based upon this report, the secondary smelter data were organized into files for the following processes:

1. Reverberatory furnaces
2. Electric induction and arc furnaces
3. Crucible furnaces
4. Pot furnaces
5. Insulated wire burners
6. Oil removal processes (dryers)

7. Rotary furnaces
8. Cupola (shaft and blast) furnaces
9. Converters (BOF)

Primary smelter data elements were also organized into files for the following operations:

1. Concentrate and flux preparation processes
2. Multiple-hearth roasters
3. Fluidized-bed roasters
4. Reverberatory smelting furnaces
5. Electric arc smelting furnaces
6. Flash smelting furnaces
7. Converters
8. Fire-refining furnaces
9. Electrolytic refining processes
10. Continuous smelting furnaces
11. Hydrometallurgical smelting processes
12. Sulfuric acid manufacturing plants

Separate files were also maintained for information on fugitive emissions and noncriteria pollutant emissions at primary and secondary smelters.

Process information in the files could be accessed without much difficulty. Project engineers began to compose the various process descriptions, and the process data appeared to be complete, current, and readily usable. In order to better organize the emission data in the files, project engineers developed a check-list for emission source test information (Figure 4-1). Recording the test results in a standardized format expedited accessing the data and simplified the task of coding. A typical example of a recorded source test report in the PES standardized format is shown in Figure 4-2. Use of this format could greatly simplify future projects in which data are to be gathered and eventually coded into

Firm's Name and Address

Source involved; contaminants involved

Process information:

- Products and production rates (specify units)
- Raw materials and charging rates (specify units)
- Maximum annual capacity (specify units)
- If batch process, maximum batch capacity (specify units)
- Typical batch time
- If continuous, maximum daily capacity
  maximum hourly capacity
- Seasonal variation (typical) in activity

Control equipment:

- Type, model, operating parameters
- Rated efficiency for various pollutants
- Configuration in relation to source

Emission point(s):

- Stack parameters
- Configuration in relation to sources and control units

Comments:

Report of source test

- Sampling position; pollutant
- Number of samples taken at this sampling position
- Fraction of batch, cycle, or day represented by sampling periods
- Weighted pollutant concentration in effluent gases
- Implied emission rates, hourly
  daily
  annually
- Implied emission factors per SCC unit
  (specify SCC unit)

Comments:

Sampling information

- Date
- Pollutant
- Sampling method
- Sampling position (related to stack, control device, and source configuration)
- Number of samples taken at this sampling position

Figure 4-1. Check List for Emission Source Information

Sample number (entry made for last sample)

Production rate and condition at time of sampling, including fuel and feed compositions if relevant
Sampling time in relation to batch, cycle, or day
Sampling period, minutes
Sampling flow rate or total volume sampled (specify)
Total pollutant found in sample (specify units)
Pollutant concentration in gas sampled (specify units)

Comments:

Figure 4-1. Check List for Emission Source Information (Concluded)

Firm: J. Doe Refining

Source: Arc furnace

Process: Producing molten high-temperature alloys
Raw materials: Cu-Ni pit scrap, iron ore, limestone, fluorspar
Maximum batch capacity: 5,000 pounds
Typical batch time: 2 hours

Control Equipment:

Baghouses: 10,000 ACFM, 2,500 fpm, 175°F
Efficiency: rated 99.9 percent
Configuration: 3 baghouses serving a swing-away hood via fixed intake point in duct above hood

Emission Point:

Stack: no data
Configuration: one of three serving baghouses

Sampling Information:

Date: 052671 Run No: 01
Sampling Position: stack top (emission control)
Production Rate: ca 20,000 pounds/day

Sample Results:

Total particulates: controlled, reported at 1.36 lb/hr; uncontrolled, reported at 2.5 lb/hr. Corresponding annual figures cited at 0.34 and 0.63 tons/yr, respectively.

Comments:

It is assumed, although not stated, that the values cited are averaged over an entire batch period. It is not clear whether more than 1 baghouse serves a single hood, and whether there are other stacks serving other baghouses.

Figure 4-2. Typical Example of Formatted Test Results

SOTDAT, since the information could be transcribed directly from the data source onto the PES form.

The task of coding the source test data into SOTDAT, while simplified by the standard test result format, still required a great deal of effort. For the most part, source test information was incomplete. Most of the reports presented only information such as pollutant tested, date of sample, measured emission rate, gas flow rate and temperature, and occasionally isokinetic sampling percentages. To provide a complete analysis, project engineers coded all tests onto SOTDAT coding forms (Ref. 19). In all, about 120 tests were coded for primary smelting sources and about 70 tests coded for secondary smelting processes.

Finally, all emission results were compiled in tables for each of the individual processes. These tables included source test results, as well as other types of emission estimates (from material balances, for instance). The results derived from these tables will be discussed in more detail in following sections for the primary and secondary smelting processes.

4.2 EMISSION FACTORS FOR PRIMARY SMELTER PROCESSES

Tables 4-1 through 4-3 present emission factors for primary copper smelting sources. All entries in the tables are given in weight of emissions per unit of concentrate which enters the smelter. The emission results are shown for various smelter configurations and for various control systems to detail the effect of these parameters on the emissions. Average emission factors for each case are unweighted, and maximum and minimum values are included to indicate the range of emissions observed.

The tables show far more tests to determine controlled emissions than uncontrolled. This is consistent with the fact that no test results were received from the smelters or from professional

Table 4-1. EMISSIONS FROM CONVERTERS IN PRIMARY COPPER SMELTERS

A. Particulates, kilograms per metric ton and pounds per ton of concentrate processed by smelter

Smelter[a] Configuration	Control[b] Equipment	Emissions				No. of Tests	No. of Plants Tested
		kg/MT		lb/ton			
		Avg.	Range	Avg.	Range		
1	0	15	11-20	30	21-40	4	1
2	0	8.5	0.7-13	17	1.4-25	4	3
All	0	12	0.7-20	24	1.4-40	8	4
1	1	1.5	0.55-3.5	2.9	1.1-6.9	14	2
1	2	0.19	0.085-0.38	0.38	0.17-0.76	7	2
2	2	0.14	0.025-0.55	0.28	0.05-1.1	19	3
3	2	0.55	0.50-0.70	1.1	1.0-1.4	3	1
All	2	0.20	0.025-0.70	0.39	0.05-1.4	29	6

[a] Configuration 1, converter follows multiple-hearth roaster and reverberatory furnace
Configuration 2, converter follows reverberatory furnace, no roaster
Configuration 3, converter follows fluidized-bed roaster and reverberatory furnace

[b] Control equipment: 0 signifies none operated
1, electrostatic precipitator
2, electrostatic precipitator with acid plant particulate control

Ref ?

Table 4-1. Continued. EMISSIONS FROM CONVERTERS IN PRIMARY COPPER SMELTERS

B. Oxides of sulfur: SO_2, and SO_3 (as H_2SO_4), in kilograms per metric ton and pounds per ton of concentrate processed.

Smelter[a] Configuration	Control[b] Equipment	Pollutant	Emissions				No. of Tests	No. of Plants Tested
			kg/MT		lb/ton			
			Avg.	Range	Avg.	Range		
1	0	SO_2	350	-	700	-	1	1
1	0	SO_3	0.65	-	1.3	-	1	1
2	0	SO_2	650	60-1,500	1,300	120-3,000	5	1
All	0	SO_2	600	60-1,500	1,200	120-3,000	6	2
1	1	SO_2	31	12-50	61	23-99	2	2
1	1	SO_3	0.07	-	0.14	-	1	1
2	1	SO_2	14	1.4-23	27	2.8-46	14	2
2	1	SO_3	0.03	0.01-0.06	0.06	0.01-0.11	13	2
All	1	SO_2	16	1.4-50	31	2.8-99	16	4
All	1	SO_3	0.04	0.01-0.07	0.07	0.01-0.14	14	3
1	2	SO_2	0.31	0.16-0.45	0.62	0.31-0.89	4	1

[a]See footnote a, Table 4-1A

[b]Control equipment: 0 signifies none operated
1 single-contact acid plant
2 double-contact acid plant

Table 4-1. Continued. EMISSIONS FROM CONVERTERS IN PRIMARY COPPER SMELTERS

C. Oxides of nitrogen (NO_x) as nitrogen dioxide (NO_2), kilograms per metric ton and pounds per ton of concentrate processed by smelter.

Smelter configuration 2: converter follows reverberatory furnace; no roaster. No control equipment operated. One test only.

Emissions		
Smelter Configuration	kg/MT Avg.	lb/ton Avg.
2	0.025	0.05

Table 4-2. EMISSIONS FROM REVERBERATORY FURNACES IN PRIMARY COPPER SMELTERS

A. Particulates, kilograms per metric ton and pounds per ton of concentrate processed by smelter.

Smelter[a] Configuration	Control[b] Equipment	Emissions				No. of Tests	No. of Plants Tested
		kg/MT		lb/ton			
		Avg.	Range	Avg.	Range		
2	0	26	21-34	52	42-67	4	2
2	1	11	0.9-34	22	1.7-68	32	3
3	1	1.2	0.13-6.5	2.4	0.25-13	18	2
All	1	7.5	0.13-34	15	0.25-68	50	5

[a]Configuration 2, converter follows reverberatory furnace, no roaster
Configuration 3, converter follows fluidized-bed roaster and reverberatory furnace.

[b]Control equipment: 0 signifies none operated
1, electrostatic precipitator

Table 4-2. Continued. EMISSIONS FROM REVERBERATORY FURNACES IN PRIMARY COPPER SMELTERS

B. Oxides of sulfur: SO_2, and SO_3 (as H_2SO_4), in kilograms per metric ton and pounds per ton of concentrate processed. No control equipment operated.

Smelter[a] Configuration	Pollutant	Emissions				No. of Tests	No. of Plants Tested
		kg/MT		lb/ton			
		Avg.	Range	Avg.	Range		
2	SO_2	115	25-310	230	50-620	19	3
2	SO_3	0.41	0-0.85	0.81	0-1.7	14	2
3	SO_2	33	19-55	66	38-110	7	1
3	SO_3	0.11	0-0.30	0.22	0-0.60	7	1
All	SO_2	110	19-310	220	38-620	26	4
All	SO_3	0.31	0-0.85	0.61	0-1.7	21	3

[a]See footnote a, Table 4-2A

C. Oxides of nitrogen (NO_x) as nitrogen dioxide (NO_2), kilograms per metric ton and pounds per ton of concentrate processed by smelter.
Smelter configuration 2: converter follows reverberatory furnace; no roaster. No control equipment operated.

Smelter Configuration	Emissions				No. of Tests	No. of Plants Tested
	kg/MT		lb/ton			
	Avg.	Range	Avg.	Range		
2	0.045	0.035-0.06	0.09	0.07-0.12	3	1

Table 4-3. COMBINED EMISSIONS FROM MULTIPLE-HEARTH ROASTERS AND REVERBERATORY FURNACES IN PRIMARY COPPER SMELTERS

A. Particulates, kilograms per metric ton and pounds per ton of concentrate processed by smelter.

Control Equipment	Emissions				No. of Tests	No. of Plants Tested
	kg/MT		lb/ton			
	Avg.	Range	Avg.	Range		
1	2.4	0.35-8.4	4.8	0.70-17	38	2
2	0.70	0.37-0.96	1.4	0.74-1.91	15	2

B. Oxides of sulfur: SO_2, and SO_3 (as H_2SO_4), in kilograms per metric ton and pounds per ton of concentrate processed. No control equipment operated.

Pollutant	Emissions				No. of Tests	No. of Plants Tested
	kg/MT		lb/ton			
	Avg.	Range	Avg.	Range		
SO_2	220	180-330	450	360-660	8	3
SO_3	0.75	-	1.5	-	1	1

organizations for use in this project. Since the majority of the tests were obtained from governmental agencies, they were primarily run for compliance determination purposes. As such, results were measured at points of emission to the atmosphere, after combining gas streams from various processes and after application of control systems.

The following specific comments apply to the information in the tables:

1. Converters

   - ESP control achieves an average control efficiency of 88 percent for particulates, while ESP's combined with the gas cleaning systems included in sulfuric acid plants yield 98 percent efficiency.
   - Particulate emissions can potentially be as high as 40 pounds per ton of concentrate and can be controlled to a level of 0.05 pounds per ton.
   - Particulate emissions from converters are potentially slightly larger in smelter configurations which include roasters.
   - SO_2 emissions are reduced by approximately 97.4 percent by single contact sulfuric acid plants, and by 99.9 percent by double contact plants.
   - Potential SO_2 emissions from converters are smaller in smelting configurations which include a roasting step.
   - Although only one test result was recorded for NO_x, it indicates that these emissions are very small.

2. Reverberatory Furnaces

   - No results were recorded for reverberatory furnaces which are operated in conjunction with a multiple-hearth roasting furnace. In all cases in this configuration, reverberatory furnace gases are combined with those of the roaster before exhausting to the atmosphere (see Roaster/Reverb).
   - SO_2 emissions from the reverberatory furnace depend on smelter configuration, since roasting will remove a portion of the sulfur in the feed to the furnace. Listed

results show that these emissions are 4 times greater when no roasting is done as compared to the case where a fluid-bed roaster is used.

- SO_2 emissions from reverberatory furnaces alone are not controlled emissions shows only 60 percent collection efficiency for an average ESP.
- Potential NO_x emissions appear to be very small, based upon a limited number of tests.

3. Multiple-Hearth Roaster/Reverberatory Furnace Combined Stream

   - As mentioned previously, test results in all of the smelters which operate multiple-hearth roasters and reverberatory furnaces were measured after the two exhaust streams had been combined and after the application of particulate control equipment.
   - At present there are no SO_2 controls applied to these gases at U.S. smelters.
   - Particulate emission factors for the combined stream cannot be analyzed into the component contributions. The reported emission factor with control by electrostatic precipitator seems inconsistent with the factor (Table 4-2) for the reverberatory furnace alone with similar control.

     One would expect the combined gases to have a higher particulate emission, but the figures indicate that the gases from the furnace alone have emissions almost 5 times greater. Both figures are based upon a comparable number of test results taken at a number of different plants. A possible explanation would be that the ESP's applied to the furnace gases were older, less efficient, or poorly maintained units.

Data items were also gathered for other emission points in the smelter, but were not sufficient to warrant tabulation. These data can be found in the background files (Ref. 20) for the following operations:

- Concentrate and Flux Preparation
- Multiple-Hearth Roasters
- Fluidized-Bed Roasters
- Electric-Arc Smelting Furnaces
- Fire-Refining Furnaces

Table 4-4 contains emission factor information which has been compiled from other data sources (Refs. 21 and 22).

4.3 EMISSION FACTORS FOR PARTICULATES FROM FURNACES USED IN SECONDARY COPPER SMELTING PROCESSES

Table 4-5 presents emission factors for particulates for secondary copper smelting sources.

The emission factors listed have been estimated from the results of source tests, or from rates of production and waste accumulation according to material-balance principles, or by other means which, in some instances, have not been identified.

Records available for inspection regarding these facilities were almost always fragmentary and unverifiable, and their interpretation in terms of emission factors therefore involved a substantial component of engineering judgment. Further, estimates regarding potential emissions from uncontrolled equipment have in some cases been estimated by applying a nominal emission control efficiency factor to the observed level of emissions from the control equipment.

Another problem was that in some of the reports of emissions tests, while it was evident that emissions measured were derived from two or more processes controlled by the same systems, it was not clear which units were being operated at the time of the test. Because of these and other difficulties, the emission factors presented can be given a rating no higher than average.

Where not otherwise specified, it is reasonable to assume that a major fraction of the particulate matter (50 percent or more) consists of oxides of heavy metals, commonly zinc, copper, lead, and tin. The detailed composition of the particulate matter is related to the composition of the material charged into the furnace; smelting of alloys containing zinc is especially likely to

Table 4-4. EMISSION FACTORS FOR SMELTER PROCESSES DERIVED FROM PUBLISHED LITERATURE

Process	Material Basis	Pollutant	Emission Factor kg/MT	Emission Factor lb/ton	Ref.
Ore Crushing	Ore	TSP	1	2	21
Roasting	Concentrate	TSP	23	45	1
	Copper	TSP	84	168	21
	Concentrate	SO_2	30	60	1
Reverberatory Furnace	Concentrate	TSP	10	20	1
	Copper	TSP	103	206	21
	Concentrate	SO_2	160	320	1
Converters	Concentrate	TSP	30	60	1
	Copper	TSP	120	235	21
	Concentrate	SO_2	435	870	1
Fire Refining	Concentrate	TSP	5	10	1
Materials Handling	Copper	TSP	5	10	21
Acid Manufacture (single-contact)	100% acid	TSP	0.6-3.7	1.2-7.4	1
		SO_2	14-35	27-70	1
		SO_2	19	38	22
(double-contact)		SO_2	2	4	1

Table 4-5. EMISSION FACTORS FOR PARTICULATE MATTER FROM FURNACES USED IN SECONDARY COPPER SMELTING AND ALLOYING PROCESSES

A. Cupolas

Type of Charge	Control[a] Equipment	Emissions kg/MT Avg.	kg/MT Range	lb/ton Avg.	lb/ton Range	No. of Units Tested	No. of Plants Tested
Scrap Copper	0	0.002	-	0.003	-	1	1
Insulated Copper Wire	0	120	-	230	-	1	1
Insulated Copper Wire	1	5	-	10	-	1	1
Scrap Copper and Brass	0	35	30-40	70	60-80	2	1
Scrap Copper and Brass	1	1.2	1.0-1.4	2.4	2.0-2.8	2	1

B. Reverberatory Furnaces

Type of Charge	Control Equipment	Emissions kg/MT Avg.	kg/MT Range	lb/ton Avg.	lb/ton Range	No. of Units Tested	No. of Plants Tested
Copper	0	2.6	0.4-15	5.1	0.8-30		12
Copper	2	0.2	0.1-0.3	0.4	0.2-0.6	2	2
Brass and Bronze	0	18	0.3-35	36	0.6-70	2	2
Brass and Bronze	2	1.3	0.03-2.5	2.6	0.05-5	2	2

[a]Control equipment: 0 signifies none operated
1 indicates electrostatic precipitator used
2 indicates baghouse filter systems

Table 4-5. Continued. EMISSION FACTORS FOR PARTICULATE MATTER AND ALLOYING FROM FURNACES USED IN SECONDARY COPPER SMELTING AND ALLOYING PROCESSES

C. Rotary Furnaces

Type of Charge	Control Equipment	Emissions				No. of Units Tested	No. of Plants Tested
		kg/MT		lb/ton			
		Avg.	Range	Avg.	Range		
Brass and Bronze	0	150	50-260	300	100-500	2	2
	1	7	3-10	13	6-19	3	3
Brass (Foundry)	0	5	-	10	-	1	1
	2	2.5	0.1-5	5	0.1-10	3	1

D. Crucible and Pot Furnaces

Type of Charge	Control Equipment	Emissions				No. of Units Tested	No. of Plants Tested
		kg/MT		lb/ton			
		Avg.	Range	Avg.	Range		
Brass and Bronze	0	11	1-20	21	2-40	17	13
	1	0.5	0.1-1	1	0.1-2	5	3

Table 4-5. Continued. EMISSION FACTORS FOR PARTICULATE MATTER AND ALLOYING FROM FURNACES USED IN SECONDARY COPPER SMELTING AND ALLOYING PROCESSES

E. Electric Arc Furnaces

Type of Charge	Control Equipment	Emissions				No. of Units Tested	No. of Plants Tested
		kg/MT		lb/ton			
		Avg.	Range	Avg.	Range		
Copper	0	2.5	1-4	5	2-8	3	2
	2	0.5	0.02-1.0	1	0.04-2	2	1
Brass and Bronze	0	5.5	2-9	11	4-18	3	2
	2	3	-	6	-	1	1

F. Electric Induction Furnaces

Type of Charge	Control Equipment	Emissions				No. of Units Tested	No. of Plants Tested
		kg/MT		lb/ton			
		Avg.	Range	Avg.	Range		
Copper	0	3.5	-	7	-	1	1
	2	0.25	-	0.5	-	1	1
Brass and Bronze	0	10	0.3-20	20	0.5-40		18
	2	0.35	0.01-0.65	0.7	0.01-1.3		6

produce large quantities of particulate matter which, in this case, contains a high proportion of zinc oxide.

Other circumstances which affect the rates of emission and the composition of the particulate matter are the type of furnace used, the operational procedures, the rate of heating and the temperature attained, the physical form of the materials fed to the furnace, and others. Available information is not sufficient to permit complete evaluation of the quantitative effects of these variables on emission rates. The emission factors listed in Table 4-5 below are, therefore, classified only with respect to the type of furnace involved and to whether the feed metal contains or does not contain zinc.

Types of furnaces encountered in secondary copper smelting are:

1. Cupola (or blast furnace)
2. Reverberatory
3. Rotary
4. Crucible (or pot)
5. Electric Arc
6. Induction (electric, high or low frequency)

The following sections discuss emission factors for furnaces of these types as indicated by emissions data and production data for both zinc-free and zinc-bearing feed metals. Where the information is available, PES reports emission factors both for actual and potential emissions, the latter corresponding to weights of material which would be emitted to the atmosphere if no emission control equipment were provided.

The following notes apply to the information shown in Table 4-5 for specific furnace types.

- Cupolas

  230 pounds per ton was estimated (by state personnel) for a smelting operation in which insulated copper wire was recycled. Presumably most of the particulate matter generated originated from the insulation materials and contained little copper oxide. An appropriate emission factor for copper oxide alone would be much smaller than 120 pounds per ton.

- Reverberatory Furnaces

  Of 12 facilities reviewed, only one indicated potential emissions larger than 10 pounds per ton.

- Rotary Furnaces

  The lower emission rates from control equipment at the foundries apparently reflect higher efficiency of control by baghouses, which were in use at some foundries, than by the equipment used at the smelters, which included scrubbers and electrostatic precipitators.

- Crucible and Pot Furnaces

  Constituents more volatile than copper included arsenic and cadmium in one case, beryllium in another. The largest factor for potential emissions occurred with a copper-arsenic alloy containing no zinc.

- Electric Arc Furnaces

  Products include refined copper (castings and shot) and various copper alloys, including bronze, tinsel bronze, beryllium copper, and high-temperature alloys containing cobalt, nickel, chromium, molybdenum, tungsten, and manganese. Beryllium emission factors appear to be about 0.002 kg/MT or 0.004 lb/short ton.

- Electric Induction Furnaces

  This table includes both high-frequency and low-frequency induction furnaces.

  Emission control was effected, in all cases cited, through the use of fabric collectors (or baghouses).

5.0 FUGITIVE EMISSIONS

5.1 INTRODUCTION

Both gaseous and particulate fugitive emissions arise from operations at primary copper smelters while those from secondary smelters are essentially limited to particulates. Generally, these emissions result from materials handling and storage, from process equipment and industrial exhaust from system leakage, and from unconfined operations such as furnace tapping and metal pouring. Problems of the respective industries are discussed below.

5.2 PRIMARY COPPER SMELTERS

5.2.1 POLLUTANTS

All the pollutants discharged from primary point sources, such as uncontrolled stacks, particulate control equipment, and acid plants, are also found as fugitive emissions. These include mechanically generated dusts from storage and transfer of ore concentrate, fluxes, and slag; metallurgical fumes from furnace operations, sulfur dioxide, and sulfur trioxide (also in form of acid fume). Table 5-1 lists many of the materials and compounds which are found as fugitive emissions.

These fugitive emissions are generally released at or near ground level and are difficult to quantify. The quantification is particularly difficult in the case of particulates because there is not good material-balance approach for estimating losses and almost no direct tests have been conducted. In the case of sulfur oxides, fugitive emissions have been estimated as the difference between the total sulfur charged to the smelting process and the total sulfur known to be collected as acid by product, discharged through stacks, and present in slag. The amount of fugitive sulfur-compound emission has been estimated by this technique to be approximately 6 percent of the total sulfur charged (Ref. 3).

Table 5-1. POSSIBLE FUGITIVE EMISSIONS FROM PRIMARY COPPER SMELTERS

Dusts

- Concentrates
- Ferric Oxide (Fe_2O_3)
- Magnetite (Fe_3O_4)
- Refractory Dust (Alumina, Magnesia)
- Slag
- Zinc Oxide (ZnO)
- Disturbed Soil

Fumes[a]

- Arsenic Trioxide (As_2O_3)[b]
- Antimony Trioxide (Sb_2O_3)[b]
- Lead Oxide (PbO)
- Zinc Oxide (ZnO)
- Sulfuric Acid Mist
- Sulfates

Gases

- Carbon Monoxide
- Sulfur Dioxide
- Nitrogen Oxides

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[a]Small amounts of other elements and compounds such as mercury, selenium, chlorides, and fluorides may be present depending upon concentrate source.

[b]Generally will condense on waste heat boilers if present.

Sometimes, primary copper smelter fugitive emissions have been characterized as "ground smoke," because of the smoky appearance or opacity of the emissions. This appearance is likely due to the presence of small aerosols, in the 0.4-1.0 micrometer diameter size range, which are very effective in scattering visible light. Many metallurgical fumes are known to be in this size range. These fume particles are small in diameter because the metals or metal oxides of which they are composed are condensed from the vapor state.

Another mechanism of "ground smoke" formation is thought to involve the reaction of a small fraction of the fugitive sulfur dioxide emissions with atmospheric oxygen to form sulfur trioxide. As the trioxide is formed it combines rapidly with water vapor to form small aerosols. This combination takes place even at low relative humidities.

The submicron sized fugitive emissions are easily capable of being transported over long distances, while at least some of the mechanically generated dusts will settle rather rapidly.

5.2.2 SOURCES

Potential sources of fugitive emissions from primary copper smelters are listed herein:

- Roaster
  Hot calcine transfer points
- Reverberatory Furnace
  Matte tap holes
  Matte launders
  Slag tap holes
  Slag skim bays
  Slag launders
  Charging points
  View ports
  Brick work leaks

- Converters
  Converter mouth
  End joints
  Hood
- Miscellaneous
  Ladles (matte and slag)
  Matte and slag handling operations
  Leaking ducts, flues, and stacks
  Other leaking process equipment
  Holding and refining furnaces

The principal source of fugitive emissions from roasters is the process of removing hot solid calcine from the roaster. Both dust and residual sulfur dioxide can be released. When the process involves dumping the calcine into cars for transfer to the reverberatory furnace, as is the case with some multiple-hearth roasters, the sudden dissipation of kinetic energy as the calcine strikes the car causes the generation of a puff of dust and trapped gases. Emissions from leaks in the roaster can also be present; the losses from fluidized-bed roasters are generally smaller than those from multiple-hearth roasters because of differences in construction. Because internal pressures are higher in fluidized-bed roasters, leakage can become significant in a fluidized-bed roaster if leakage points exist.

Reverberatory furnaces produce molten matte from either "green" charge or calcine. Charging and tapping of the furnace for the matte both are carried out intermittently while melting continues. Even though the furnace operates at slightly less than atmospheric pressure (generally about -0.05 to -0.1 inch w.c.), the charging operation is conducted through openings in the furnace from which some dust, fume, and sulfur dioxide may escape.

Molten matte is removed from the furnace through tap holes which are normally plugged. During tapping these are opened and the

matte flows through channels called launders to ladles. Most furnaces have two or three matte tap holes on each side. Because the matte is still close to furnace temperature as it is removed, the remaining sulfur in the form of sulfides can continue to oxidize outside the furnace for a time, forming sulfur dioxide. Oxides of volatile metals may also be emitted from the launders and the ladle. As the ladle is transported to the converters, emissions can continue. These emissions produce the earlier-described ground smoke. The less dense slag which floats on top of the matte in the reverberatory furnace is also removed periodically through slag tap holes and launders. Some emissions result from this operation but they are not generally as intense as those from the matte.

Reverberatory furnaces are constructed of refractory bricks. Because of the need to allow room for thermal expansion, it is difficult to achieve a leakproof condition. Also, in the case of furnaces built with suspended roofs, a gap exists between the furnace walls and the roof which must be packed with a heat-resistant material. Any imperfections in this packing will result in leak points. The sealing problem is not as difficult with sprung-arch roof construction. Leaks may be sealed by spraying on a slurried refractory.

Fugitive emissions associated with copper converting generally result from ineffective capture of fumes and sulfur dioxide during certain phases of the converter operation. During blowing, the exhaust hood placed over each converter generally fits rather tightly and emissions are exhausted with little loss. The fit is not perfect, however, as there must be some gap between the hood and the opening to prevent freezing of the hood to the converter as a consequence of splashing of molten copper. A chain-curtain closure is sometimes used at the edge of the hood to minimize the opening while still providing

durability and flexibility. A metal skirt is sometimes used to improve the seal and minimize deterioration of the converter. In a properly designed system it is possible to collect nearly all the emissions during the "roll-in" and blowing phase.

Automatic damper controls are generally used to prevent excess dilution air from being drawn into the system while at the same time maintaining effective fume collection from most phases of converter operation. If the damper control point is improperly set or if the charge level in the converter is higher than normal, fugitive emissions can result.

When the converter is rolled out for pouring either slag or blister copper, the hood draft is usually shut off by dampers. The main reason for this is to maintain a higher concentration of sulfur dioxide in gases that are fed to the by-product acid plant (if such a plant is provided). When the dampers are closed the converter emissions are uncaptured and discharged directly to the atmosphere. The roll-out operational phase can amount to 3 to 6 hours out of every 24-hour period for each converter.

A variety of other fugitive emission sources can be present in a smelter, most of which involve leaks in waste heat boilers, heat exchangers, and flues and ducts. Another minor source of fugitive emissions is fire refining. The residual sulfur content of blister copper is only about 2 percent and any small amounts of impurities remain. Therefore, when final blowing is conducted the potential quantity of emissions is small. These furnaces are, therefore, not hooded and any emissions resulting from the operation can be classified as fugitive.

5.3 SECONDARY COPPER SMELTERS

Fugitive emissions from secondary copper smelters are generally limited to dusts, fumes, and smoke because the sulfur content of the

scrap charge is very low. As in the case of primary smelters, larger particulates classified as dust can be expected from materials handling and from furnace charging. Because these materials settle rather rapidly, the impact depends upon how well these operations are protected from the wind.

The other fugitive emissions result from uncaptured or uncontrolled contaminants generated by the furnaces. These include metal fumes (zinc and other volatile metal oxides) and smoke from oily or insulation-covered scrap. Most of these emissions arise during charging, slag removal, metal tapping or pouring, chage mixing, and air lancing. Because a wide variety of furnace types are used, hood design and effectiveness can vary substantially.

5.4 FUGITIVE EMISSION CONTROL

Fugitive emissions control techniques can be divided into two major categories: (1) process changes to eliminate or minimize generation of emissions, and (2) installation of equipment to collect the emissions. A requirement in either case is that process equipment and industrial ventilation be designed and maintained to control leakage.

In primary copper smelting, several types of process changes are possible. To reduce emissions while charging reverberatory furnaces, automatic control of furnace pressure could be incorporated. This could involve the installation of pressure transducers to produce a signal which would control dampers or fans to maintain the desired negative pressure. In the case of converters, techniques might be devised to reduce the time during which the converter opening is rolled out away from the hood opening. Fluidized-bed roasters could be substituted for multiple-hearth roasters.

Installation of additional or improved systems for collecting emissions would involve changes in some present industry practices.

At present most furnace operations are located in large buildings with some open sides and openings (monitors or other vents) in the roof. Installation of additional hoods and ventilation equipment could be complicated by existing support structures and cranes. On the other hand, reduction of emissions inside these buildings could improve the work environment.

The collection of fugitive emissions does not necessarily mean that all current discharge of fugitive emissions would be eliminated. The actual reduction of emissions would be influenced by the overall abatement plan for each source and applicable regulations. In the case of collected but uncontrolled emissions, it is still likely that ambient pollutant concentrations would be reduced because of the discharge through elevated stacks in place of ground level discharge.

Table 5-2 summarizes fugitive emission points, quantities emitted, and possible control techniques for primary copper smelting sources. While controls for secondary smelters have not been directly discussed in this section, many of the same techniques considered for primary smelters would be applicable.

Table 5-2. FUGITIVE EMISSION SOURCE, QUANTITY AND CONTROL

Fugitive Emission Source	Quantity Emitted	Control
Roaster Hot Calcine Transfer Points	Minor	Evacuated room-type enclosure
Roaster Leakage	Major (possibly)	Repair or replace
Furnace Matte Taps and Launders	Major	Evacuated room-type enclosure or separate evacuated hoods
Furnace Slag Taps, Launders, and Skim Bay	Significant but not as great as from matte	Separate evacuated hoods
Furnace Charging Points and Leaks	Major (possibly)	a. Pressure control systems to maintain negative pressure at all times b. Reduce firing rate during charging
Converter Mouth	Major	a. Separate hood and evacuation system b. Completely enclose converter with removable hood c. Feed cold materials through hood
Converter End Leakage	Major (possibly)	Repair
Ladles - Matte and Slag Handling	Major	Hoods at launder pouring points
Leakage at Ducts and Equipment	Major (possibly)	Continuous maintenance and repair

6.0 RECOMMENDATIONS FOR FURTHER SOURCE TESTING

Both the primary and secondary copper smelting industries involve a rather wide variety of processes and equipment types. In the case of primary copper smelting the sulfur content of the ore varies significantly. In the secondary smelting industry the nature and composition of scrap feed varies widely. An attempt was made to develop emission factors for the major processes and combinations of processes in these industries. Insufficient valid test data were available to cover all the possibilities of feed composition, nature of specific process or equipment, and type of air pollution; therefore accurate emission factors could not be developed for all these combinations. Many tests had been done, but often important data elements were missing, such as feed rate or composition. Another complication with primary smelters is that tests were performed on combined gas streams and not on streams from individual items of equipment.

Because of these difficulties, it was decided that emission factors for uncontrolled sulfur dioxide emissions should be based upon an average sulfur content in copper concentrate and on a distribution of this sulfur found in a large number of tests. The sulfur content used is specified so that corrections can be made where sulfur content differs and is known. However, there are only 15 primary copper smelters in the United States, each one having a different configuration. Therefore, these emission factors should probably not be used to estimate potential emissions from any given plant. (Latest data specific to the plant should be used instead.)

Emission factors for particulates and for controlled emissions must be based upon testing. As will be discussed in more detail in this section, it is obvious that a major program of testing smelter sources is needed if precision and accuracy of these factors is to be improved.

6.1 PRECISION OF EMISSION FACTORS

To formulate any program to supplement the existing tables of emission factors, it is important to examine the precision of the data in those tables. A system for examining precision has been promulgated by EPA. Called "Source Inventory and Emission Factor Analysis" (SIEFA), it is intended to provide estimates of the precision of all the elements of an emissions inventory, including, in particular, the emission factors which may be necessary in quantifying industrial emissions.

Tables 6-1 and 6-2 provide estimates of standard deviation and precision for the emission factors (presented in Section 4.0) for primary copper smelting processes. For particulate emissions, estimates of the precision of the emission factors range from 0.07 to 0.34; that is, the standard error of the emission factor is between 7 and 34 percent of the factor. (The standard error is equal to the standard deviation divided by the square root of the number of observations accepted.) For sulfur dioxide emission factors, precision estimates range from 0.09 to 0.78 - somewhat larger, on the whole, than those for particulates.

Considered solely in the light of these precision estimates, it may be reasonable to suggest that additional attention be directed toward those factors with precision poorer - i.e., larger - than 25 percent. These would include uncontrolled particulate emissions from converters in the configuration, reverberatory furnace followed by converter, and from reverberatory furnaces in another smelter configuration; also, sulfur dioxide emissions uncontrolled and from single-contact acid plants.

However, the precision of the emission factor is not usually the most important error-bearing item in determining the accuracy of emission estimates, since the precision is, basically, independent of accuracy. That is, an estimate can be quite precise

Table 6-1. SIEFA STANDARD DEVIATIONS AND PRECISION FACTORS FOR PRIMARY COPPER SMELTING PROCESSES (PARTICULATE EMISSIONS)

Process Unit	Smelter[a] Configuration	Control[b] Equipment	E.F. kg/MT	S.D. kg/MT	E.F. lb/ton	S.D. lb/ton	Estimated Precision
Converter	1	0	15	4.6	30	9.2	0.15
	2	0	8.5	5.8	17	11.5	0.34
	1	1	1.5	0.75	2.9	1.5	0.13
	1	2	0.19	0.11	0.38	0.22	0.22
	2	2	0.14	0.14	0.28	0.28	0.23
	3	2	0.55	0.13	0.11	0.25	0.13
Reverberatory Furnace	2	0	26	6.1	52	12.1	0.12
	2	1	11	6.9	22	13.7	0.11
	3	1	1.2	1.8	2.4	3.5	0.34
Combined Stream of Roaster and Reverberatory Furnace	1	1	2.4	1.7	4.8	3.3	0.11
	1	2	0.7	0.19	1.4	0.37	0.07

[a]Configuration 1, converter follows multiple-hearth roaster and reverberatory furnace
Configuration 2, converter follows reverberatory furnace, no roaster
Configuration 3, converter follows fluidized-bed roaster and reverberatory furnace

[b]Control equipment: 0 signifies none operated
1, electrostatic precipitator
2, electrostatic precipitator with acid plant particulate control

Table 6-2. SIEFA STANDARD DEVIATIONS AND PRECISION FACTORS FOR PRIMARY COPPER SMELTING PROCESSES (SULFUR DIOXIDE EMISSIONS)

Process Unit	Smelter[a] Configuration	Control[b] Equipment	E.F. kg/MT	S.D. kg/MT	E.F. lb/ton	S.D. lb/ton	Estimated Precision
Converter	1	0	350	-	700	-	0.25
	2	0	650	620	1,300	1,240	0.42
	1	1	31	33.7	61	67.4	0.78
	2	1	14	6.7	27	13.4	0.13
	1	2	0.31	0.14	0.62	0.28	0.23
Reverberatory Furnace	2	0	140	96	280	191	0.16
	3	0	33	13.3	66	26.6	0.15
Combined Stream of Roaster and Reverberatory Furnace	1	0	230	53	450	106	0.09

[a]Configuration 1, converter follows multiple-hearth roaster and reverberatory furnace
Configuration 2, converter follows reverberatory furnace, no roaster
Configuration 3, converter follows fluidized-bed roaster and reverberatory furnace

[b]Control equipment: 0 signifies none operated
1, single-contact acid plant
2, double-contact acid plant

and nevertheless wrong, because of errors and uncertainties not related to precision. In particular, with respect to sulfur emissions, a large and irreducible source of variation in uncontrolled emissions can be due to variations in the composition of the ore or other feed material. It follows that, for improved accuracy, sulfur emissions should be expressed in relation to composition of the feed. Although emissions from fuel-burning have long been routinely expressed in this manner, emissions from copper smelters have not been so expressed.

Unfortunately, the data made available to PES in this project were far too fragmentary to permit the utilization or even exploration of this approach. None of the data for this study were furnished directly by smelter firms. Nevertheless, it seems likely that some smelter companies may have obtained such data for their own use in private studies unrelated to air quality compliance testing. Tests conducted to verify control equipment efficiencies, for example, would be very valuable as a supplement to the existing data base.

Of interest as indicating a special need for new source tests is a recently discovered problem relating to sulfur compounds in the copper smelter stack gases and their relationship to the measurement of particulate matter. When compliance tests were performed on primary smelters in Arizona in late 1975 (Ref. 23), it was found that the EPA Method 5 test for determination of particulate matter suffered serious interference from sulfuric acid mist which condensed in the probe and filter holder or passed through the filter as a mist. Two questions arose from this circumstance. First, should this acid material be counted as particulate matter? This would depend on whether the material was in a gaseous form in the stack and was later condensed in the probe and filter or whether it was in the form of acid mist, which is considered particulate. Second, how can reproducibility in the use of Method 5 be assured?

With this volatile material condensing in the testing apparatus it was difficul· ·if not impossible, to secure reproducible test results.

A joint research program is being carried out by the Arizona Bureau of Air Quality Control (Ref. 24), the Magma Copper Company, and the Phelps Dodge Corporation to discover some method of testing which will separate, quantify, and identify the condensible and solid particulate matter.

6.2 RECOMMENDATIONS FOR ADDITIONAL TESTING

Based on scrutiny of the emission factors reported above, together with consideration of the estimated precision of those factors and the application of engineering judgment, it is recommended that the processes listed in Table 6-3 be studied. Particular attention should be given to the problem of determining potential uncontrolled emissions, i.e., the emissions which would enter the atmosphere if no control systems were in use. Table 6.2-1 also lists primary smelter plants which are known to operate the particular processes mentioned and which might, therefore, be considered as possible test sites.

Additional testing would also be desirable for secondary copper smelting and alloying plants. Because of the large number of plants in the United States the development of statistically valid average emission factors for various types of furnaces seems appropriate. The priority of this work will have to be determined in consideration of available resources and the impact of any improvement in factor accuracy that might result.

Determination of fugitive emissions represent yet another problem, regarding which little information is available. Because of the difficulty of measuring them, little effort has been made by the industry to quantify these emissions. Sulfur dioxide

Table 6-3. PRIMARY COPPER SMELTING PROCESSES FOR WHICH EMISSION FACTORS SHOULD BE DEVELOPED

Process	Pollutant to be Tested	Possible Test Sites
Concentrate and Flux Crushers	Particulates	Kennecott, Hayden, Arizona and others
Multiple-Hearth Roasters	Particulates and SO_2	1. ASARCO, Tacoma, Washington 2. ASARCO, Hayden, Arizona 3. ASARCO, El Paso, Texas 4. Phelps Dodge, Douglas, Arizona
Fluidized-Bed Roasters	Particulates and SO_2	1. Phelps Dodge, Morenci, Arizona 2. Kennecott, Hayden, Arizona 3. Anaconda, Anaconda, Montana 4. Cities Service, Copperhill, Tennessee
Electric-Arc Smelting Furnaces	Particulates and SO_2	1. Cities Service, Copperhill, Tennessee 2. Inspiration, Miami, Arizona
Flash Smelting Furnaces	Particulates and SO_2	Kennecott, Hurley, New Mexico
Anode Furnaces	Particulates	ASARCO, Tacoma, Washington, and others

fugitive emissions are usually estimated by a material balance. All measurable sulfur outputs are summed and compared to the total sulfur input, with the difference being assumed to represent fugitive emissions.

Three basic strategies can be considered for sampling of fugitive emission sources. These strategies, in order of decreasing probable accuracy, are:

1. Mock-up Stack: Emissions are captured in a temporary hood-duct-fan system and measured by essentially standard stack sampling methods.
2. Roof Monitor: Roof monitors and other vent openings in buildings containing fugitive emissions are evaluated with appropriate instrumentation to determine airflows and material balances through these openings.
3. Environmental Sampling: Outdoor air is monitored during prescribed meteorological conditions using a network of sampling sites upwind and downwind of the source to determine pollutant flux.

Of these three approaches, the first is preferred from an engineering standpoint because it offers the most direct and verifiable accounting for the effluents to be measured. At the same time, it requires the highest degree of cooperation and assistance from the smelter operating staff and causes the greatest difficulties in avoiding interference with normal process operations. Sampling at roof monitors is less direct and more difficult, but involves less interference with plant operations. Outdoor sampling is typically a last-resort measure, which would only be attempted if it were necessary to estimate emissions from a plant to which no access could be obtained; very low accuracy would be expected from this technique.

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APPENDIX A

SECTION 7.3
PRIMARY COPPER SMELTING

Prepared by

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EPA Contract No. 68-02-1890

Task Order No. 3

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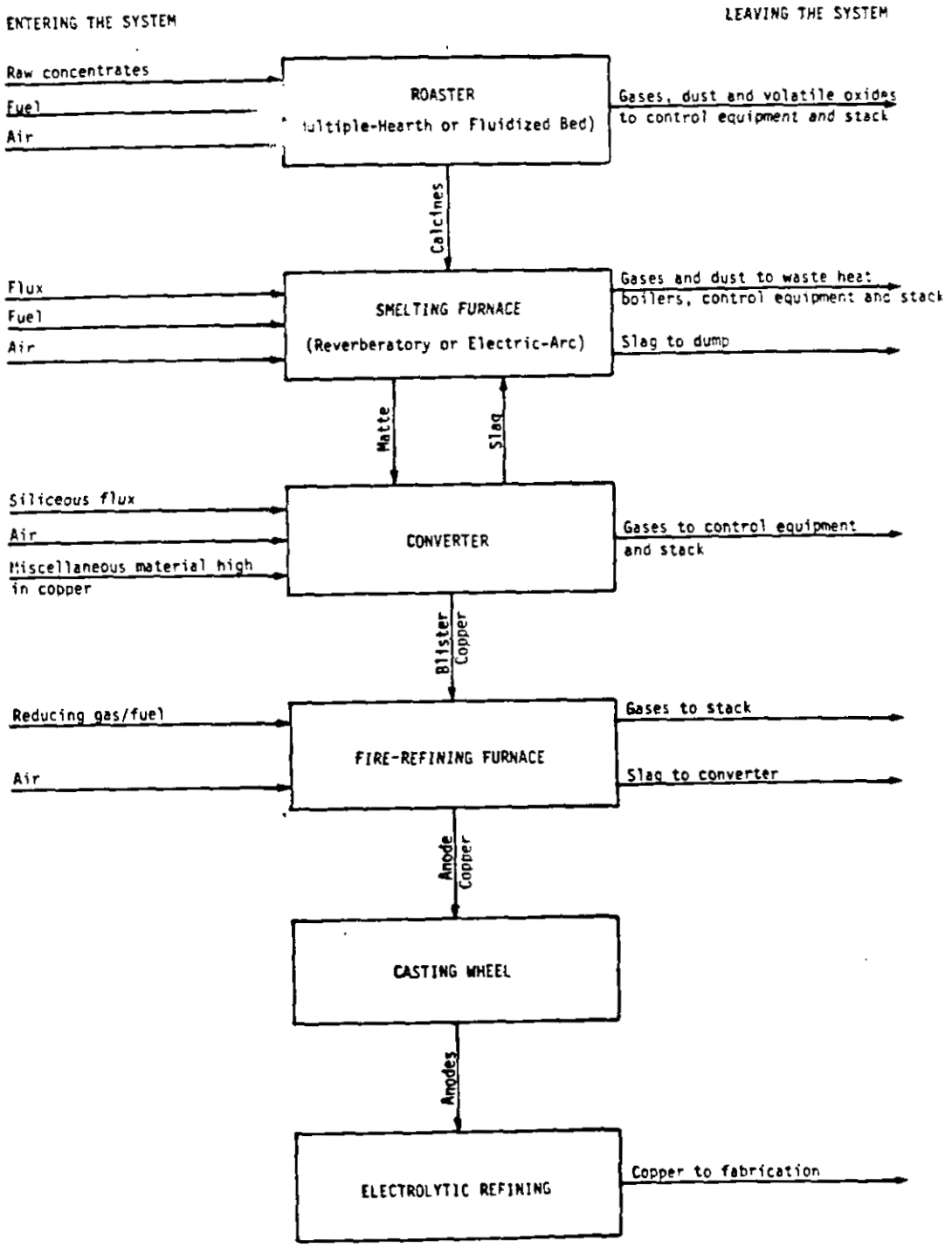

Figure 7.3-1. Typical Primary Copper Smelter Flowsheet

flux (often a low-grade ore) to produce the roaster charge material. The roasted product, called calcine, serves as a dried and preheated charge for the smelting furnace. Either multiple-hearth or fluidized-bed roaster furnaces are used for roasting copper concentrate. Because there is less air dilution, higher SO_2 concentrations are present in fluidized-bed roaster gases than in multiple-hearth roaster gases.

The second step is smelting. In this process, hot calcines from the roaster, or raw, unroasted concentrate are fused with limestone and siliceous flux, in reverberatory or electric-arc furnaces, to produce copper matte. Copper matte is primarily miscible liquid sulfides and some heavy metals. In reverberatory furnace operation, heat is supplied by combustion of oil, gas, or pulverized coal, and is reflected from the roof of the furnace onto the charge. As the charge is melted, copper, iron, and sulfur form cuprous sulfide (Cu_2S) and ferrous sulfide (FeS). Other minerals combine with fluxes forming slag. Slag floats on top of the molten bath and is removed continuously. Copper matte remains in the furnace until poured. Normal smelting furnace operations produce a matte which contains 40- to 45-percent copper.

For smelting in electric-arc furnaces, heat is generated by an electric current passing through carbon electrodes which are lowered into the slag layer of the molten bath. Electric furnaces do not produce fuel combustion gases, therefore, gas flow rates are lower and SO_2 concentrations are higher in electric furnace effluent streams than those in reverberatory furnace gases.

The final step in the production of blister copper is converting. Converting is normally performed in Peirce-Smith converters. The converter consists of a cylindrical steel shell. The shell is mounted on trunnions at either end and rotated about its major axis. An opening in one side of the converter functions

as a mouth through which molten matte, siliceous flux, and scrap copper are charged to the converter and gaseous products are vented. Air or oxygen-enriched air is blown through the metal; FeS is oxidized and combined with the flux to form a slag which floats on the surface. Relatively pure Cu_2S (called "white metal") is collected in the bottom of the converter. After removal of slag, a renewed air blast oxidizes the sulfide sulfur to SO_2 leaving blister copper in the converter.

Hoboken converters have recently been installed at one U.S. smelter to replace the standard Peirce-Smith converters. The metallurgical operations of the Hoboken unit are the same as those of the Peirce-Smith unit. However, to prevent dilution air from entering the exhaust gas stream, the Hoboken converter is fitted with a stationary side flue instead of a movable hood.

In a newer process, roasting and smelting are combined in one operation to produce a high-grade copper matte from concentrates and fluxes, using a flash furnace. Fuel is supplied to sustain combustion reactions, but most of the heat necessary for smelting is generated autogenously by the oxidation of the sulfides in the concentrate.

The flash smelting operation has also been applied to the oxidation of matte to blister copper in the continuous smelting process. Continuous smelting systems which have been operated at foreign smelters include the Noranda, WORCRA, Mitsubishi, and TBRC (top-blown rotary converter) processes.

Blister copper usually contains from 98.5- to 99.5-percent pure copper. Impurities may include gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, tellurium, and zinc. To further purify the blister copper, fire refining and electrolytic refining are used. In fire refining, air is blown through the metal to oxidize remaining impurities; these

are removed as a slag, and the remaining metal bath is subjected to a reducing atmosphere to reconvert cuprous oxide to copper. The fire-refined copper is cast into anodes and further refined electrolytically.

Electrolytic refining involves separation of copper from impurities by electrolysis in a solution containing copper sulfate and sulfuric acid. Metallic impurities precipitate from the solution and form a sludge which is removed and treated for recovery of precious metals. The copper produced is 99.95- to 99.97-percent pure.

Hydrometallurgical processes are usually applied to recovery of copper from oxide ores, but their application in U.S. plants is limited.

7.3.2 Emissions and Controls

Particulates and sulfur dioxide are the principal air contaminants emitted at primary smelters. In some cases, these emissions are generated directly as a result of the processes involved, as in the liberation of sulfur from the ore as SO_2 emissions, or the volatilization of trace elements to oxide fumes. Significant quantities of fugitive emissions are generated from material handling operations and during the charging and tapping of furnaces. Actual quantities of emissions from a particular smelter unit depend upon the configuration of equipment in the smelting plant and the operating parameters employed. Table 7.3-1 summarizes the emission factors for the major units for various smelter configurations. Other potential emission sources, which have not been quantified, include ore crushing and preparation, flux crushing, ore storage, concentrate drying, slag dumping, fire refining, and copper casting.

Table 7.3-1. EMISSION FACTORS FOR PRIMARY COPPER SMELTERS[a,d]

Smelter configuration	Unit	Control[b]	Particulates[c]		SO_2[c]		SO_3 (as H_2SO_4)[c]		NO_x (as NO_2)[c]	
			lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Reverberatory furnace followed by converters	Reverb.	None	36	18	390	195	0.81	0.41	0.09	0.045
		ESP	22	11						
	Converter	None	42	21	860	430	-		0.05	0.025
		ESP	2.5	1.3			-			
		ESP + SCAP	0.28	0.14	27	14	0.06	0.03		
Multiple-hearth roaster followed by reverberatory furnace and converters	Roaster	None	45	22.5	410	205	-		-	
		Baghouse	0.2	0.1	-		-		-	
	Roaster and reverb.[e]	None	-		450	230	1.5	0.75	-	
		ESP	4.8	2.4					-	
		Spray Chamber + ESP	1.4	0.7					-	
	Converter	None	42	21	540	270	-		-	
		ESP	2.9	1.5			-		-	
		ESP + SCAP	0.38	0.19	61	31	0.14	0.07	-	
		ESP +	0.38	0.19	0.62	0.31	-		-	
Fluidized-bed roaster followed by reverberatory furnace and converters	Reverb.	ESP	2.4	1.2	66	33	0.22	0.11	-	
	Roaster	None	55	28	540	270	-		-	
		Baghouse + SCAP	0.1	0.5	2	1	-		-	
	Converter	ESP + SCAP	1.1	0.55	-		-		-	
Fluidized-bed roaster followed by electric furnace and converters	Roaster	None	55	28	540	270	-		-	
		Baghouse + SCAP	0.1	0.05	2	1	-		-	
	Electric furnace	None	-		131	66	-		-	
	Converter	None	-		444	72	-		-	
Total uncontrolled smelter		None	135	66.5	1,254	627	-		-	

[a] Emission factors are expressed as units per unit weight of concentrated ore processed by the smelter. Approximately 4 unit weights of concentrate are required to produce 1 unit weight of copper metal.

[b] ESP = electrostatic precipitator
SCAP = single contact acid plant
DCAP = double contact acid plant

[c] References 2, 4, 5, 6, 7, and 9. Additional information was furnished by the following agencies:
Arizona Department of Health Services, Phoenix, Arizona
Montana State Department of Health and Environmental Sciences, Helena, Montana
Puget Sound Air Pollution Control District, Seattle, Washington
New Mexico Environmental Improvement Agency, Santa Fe, New Mexico

[d] Ore storage, crushing and handling; flux crushing and handling; concentrate drying and handling; slag dumping; fire refinery and copper casting are potential emission sources but emission rates have not been quantified.

[e] Roaster and reverberatory furnace emissions are combined and therefore a single set of emission factors is provided.

Multiple-hearth and fluidized-bed roasters are sources of both particulates and sulfur oxides. Particulates consist of oxides of the metals which are found in the concentrate. Copper and iron oxides are the primary constituents, but other oxides such as those of arsenic, antimony, cadmium, lead, mercury, and zinc may also be present with metallic sulfates and sulfuric acid. Combustion products from fuel burning also contribute to the particulate emissions from multiple-hearth roasters. It is standard practice in the industry to control particulates from roaster gases because of the recovery value of the copper in the dust and because of the presence of toxic particulates such as arsenic. Cyclones and scrubbers may be used for coarse particulate removal and are usually followed by electrostatic precipitators (ESP's) or fabric filters for collection of fines.

Smelting furnaces also emit significant quantities of oxidized metal particulates and SO_2. Particulate collection systems for smelting furnaces are similar to those used for roasters. Reverberatory furnace offgases are usually routed through low-velocity balloon flues and waste heat boilers to recover large particles and heat, then routed through electrostatic precipitators. Overall collection efficiencies of 95 to 99 percent for ESP systems are normal for these applications. Efficiencies as high as 99.7 percent have been reported.

Converter flue gases also contain particulates and SO_2. In the standard Peirce-Smith converter, flue gases are captured during the blowing phase by movable hooding which covers the converter mouth opening. To prevent freezing of the hood to the converter (caused by splashing of molten metal), there is a gap between the hood and the vessel. Sophisticated draft control devices have been developed which maintain a negative pressure at the gap to draw air in for cooling and to prevent fugitive

emissions. During charging and pouring operations, significant fugitive emissions may occur when the hooding is removed to allow crane access.

Remaining smelter processes handle material which contains very little sulfur. Hence, SO_2 emissions from these processes are relatively insignificant. Particulate emissions from fire-refining operations, however, may still be of concern. Electrolytic refining does not produce emissions unless the associated 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.

Control of SO_2 emissions from smelter sources is most commonly performed in a single or double-contact sulfuric acid manufacturing plant. Use of a sulfuric acid plant on copper smelter effluent gas streams requires that gas be free from particulate matter and that a certain minimum SO_2 concentration be maintained. Table 7.3-2 shows typical average SO_2 concentrations for the various smelter unit offgases. These offgas streams may be treated individually, or weak and strong concentration streams may be blended. Typically, single-contact acid plants achieve 96.5- to 97-percent conversion of SO_2 to acid with approximately 2,000 parts per million (ppm) of SO_2 remaining in the acid plant effluent gas. Double-contact acid plants collect 98 percent of the SO_2 and emit about 500 ppm SO_2. Absorption of the SO_2 in dimethylaniline (DMA) solution has also been used in U.S. smelters for production of liquid SO_2.

Emissions from hydrometallurgical smelting plants are generally small in quantity and easily controlled. In the Arbiter process, ammonia gas escapes from leach reactors, mixer-settlers, thickeners, and tanks. For control, all of these units are covered and vented to a packed-tower scrubber which recovers the ammonia and recycles it.

Table 7.3-2. AVERAGE SO_2 CONCENTRATIONS IN OFFGASES FROM PRIMARY COPPER SMELTING SOURCES

Unit	$\%SO_2$
Multiple-Hearth Roaster	1.5-3
Fluidized-Bed Roaster	10-12
Reverberatory Furnace	0.5-1.5
Electric-Arc Furnace	4-8
Flash-Smelting Furnace	10-20
Continuous Smelting Furnace	5-15
Peirce-Smith Converter	4-7
Hoboken Converter	8
Single Contact H_2SO_4 Plant	0.2
Double Contact H_2SO_4 Plant	0.05

No control practices are currently utilized in U.S. smelters for NO_x, CO, or hydrocarbon emissions, which are found in the offgas streams from units requiring fuel combustion. Multiple-hearth roasters, reverberatory furnaces, converters, and refining furnaces are sources of these contaminants. Data are available for assigning emission factors for NO_x emissions from reverberatory furnaces and converters in only one smelter configuration (Table 7.3-1). Data for assigning emission factors for CO and hydrocarbons are unavailable.

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APPENDIX B

SECTION 7.9
SECONDARY COPPER SMELTING AND ALLOYING

Prepared by

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7.9 SECONDARY COPPER SMELTING AND ALLOYING

7.9.1 Process Description

The secondary copper industry processes scrap metals for the recovery of copper. Products include refined copper or copper alloys in forms such as ingots, wirebar, anodes, and shot. Copper alloys are combinations of copper with other materials, notably, tin, zinc, and lead. Also, for special applications, combinations include such metals as cobalt, manganese, iron, nickel, cadmium, and beryllium and nonmetals such as arsenic and silicon.

The principal processes involved in copper recovery are scrap metal pretreatment and smelting. Pretreatment includes cleaning and concentration processes necessary to prepare the material for the smelting furnace. Smelting involves heating and treating the scrap to achieve separation and purification of specific metals.

The feed material used in the recovery process can be any metallic scrap containing a useful amount of copper, bronze (copper and tin), or brass (copper and zinc). Traditional forms are punchings, turnings and borings, defective or surplus goods, metallurgical residues such as slags, skimmings, and drosses, and obsolete, worn out, or damaged articles including automobile radiators, pipe, wire, bushings and bearings.

The type and quality of the feed material determines the processes the smelter will use. Due to the large variety of possible feed materials available, the method of operation varies greatly between plants. Generally, a secondary copper facility deals with less pure raw materials and produces a more refined product, whereas brass and bronze alloys processors take cleaner scrap and do less purification and refining. A flowsheet depicting the major processes that can be expected in a secondary copper

smelting operation is shown in Figure 7.9-1. A brass and bronze alloying operation is shown in Figure 7.9-2.

Pretreatment of the feed material can be accomplished using several different procedures, either separately or in combination. Feed scrap is concentrated by manual and mechanical methods such as sorting, stripping, shredding, and magnetic separation. Feed scrap is sometimes briquetted in a hydraulic press. Pyrometallurgical pretreatment may include sweating, burning of insulation (especially from wire scrap), and drying (burning off oil and volatiles) in rotary kilns. Hydrometallurgical methods include flotation and leaching, with chemical recovery.

In smelting, low-grade scrap is melted in a cupola furnace, producing "black copper" (70- to 80-percent Cu) and slag; these are often separated in a reverberatory furnace, from which the melt is transferred to a converter or electric furnace to produce "blister" copper which is 90- to 99-percent Cu.

Blister copper may be poured to produce shot or castings, but is often further refined electrolytically or by fire refining. The fire-refining process is essentially the same as that described in the primary copper smelting industry (refer to Section 7.3.1). sequence of events in fire-refining is (1) charging; (2) melting in an oxidizing atmosphere; (3) skimming the slag; (4) blowing with air or oxygen; (5) adding fluxes; (6) "poling" or otherwise providing a reducing atmosphere; (7) reskimming; and (8) pouring.

To produce bronze or brass rather than copper, an alloying operation is required. Clean, selected bronze and brass scrap is charged to a melting furnace with alloys to bring the resulting mixture to the desired final composition. Fluxes are added to remove impurities and to protect the melt against oxidation by air. Air or oxygen may be blown through the melt to adjust the composition by oxidizing excess zinc.

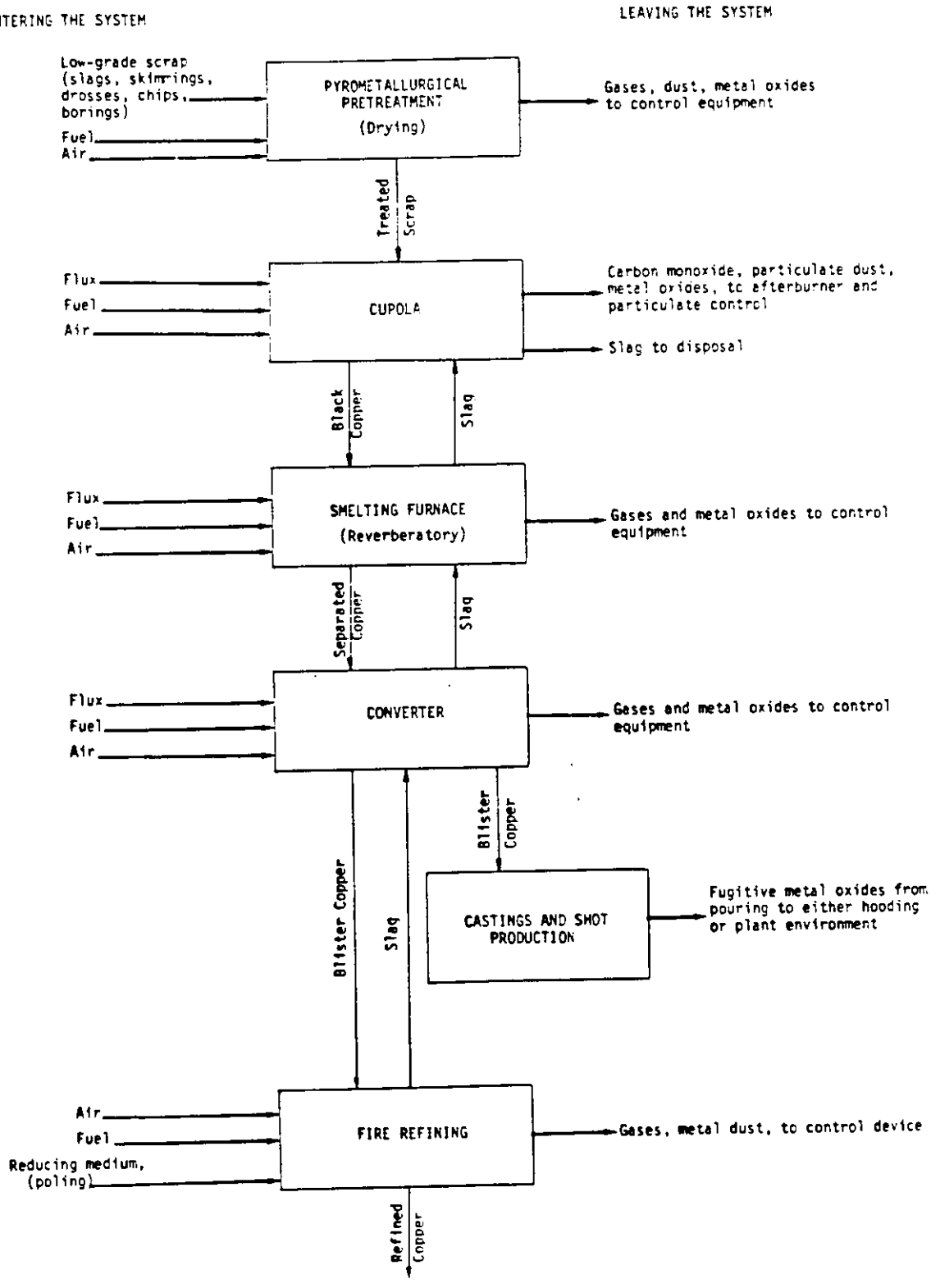

Figure 7.9-1. Low-Grade Copper Recovery

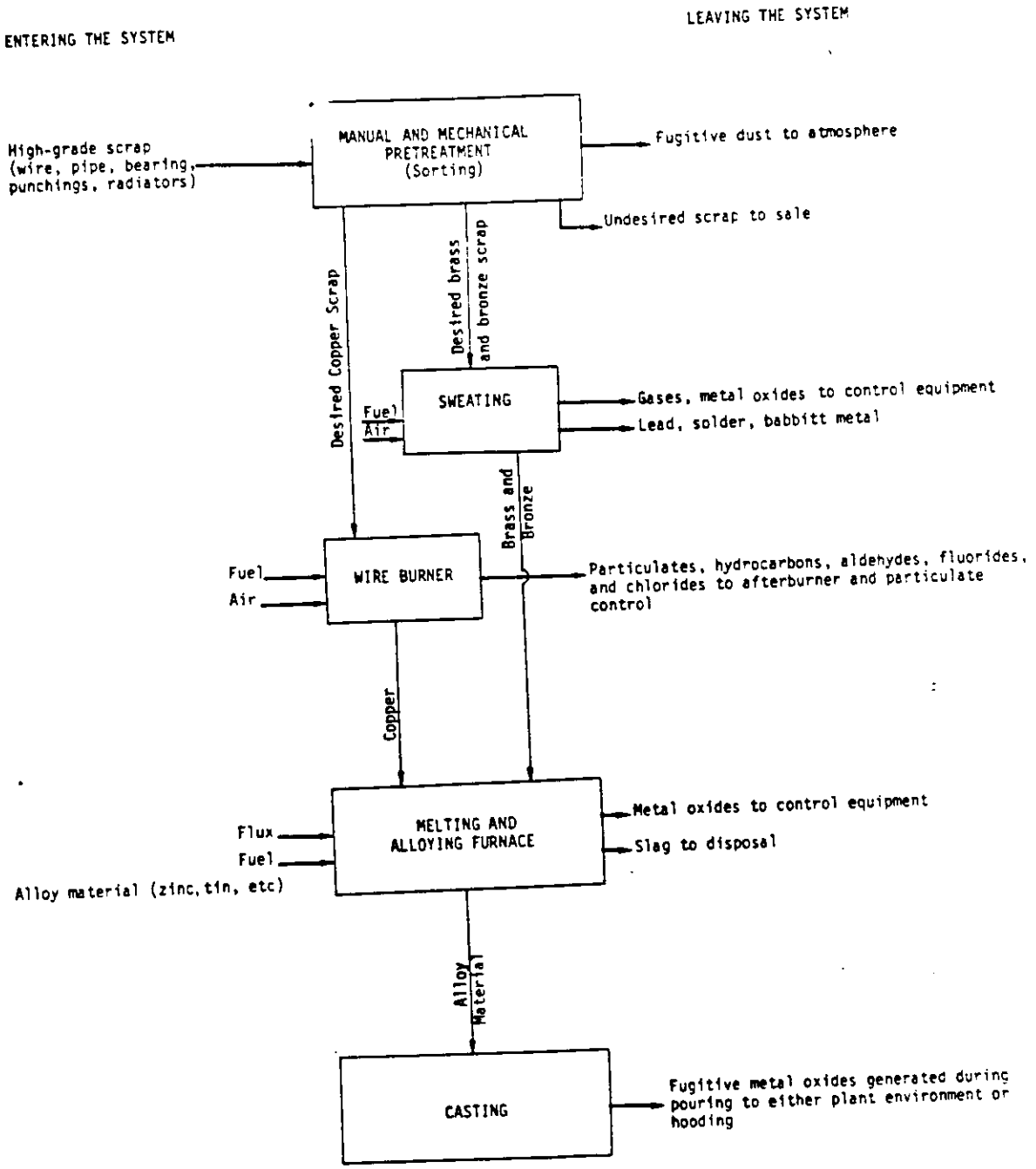

Figure 7.9-2. High-Grade Brass and Bronze Alloying

With zinc-rich feed such as brass, the zinc oxide concentration in the exhaust gas is sometimes high enough to make recovery for its metal value desirable. This process is accomplished by vaporizing the zinc from the melt at high temperature and capturing the oxide downstream in a process baghouse.

The final step is always casting of the suitably alloyed or refined metal into a desired form. This form may be shot, wirebar, anodes, cathodes, ingots, or other cast shapes. The metal from the melt is usually poured into a ladle or a small pot, which serves the functions of a surge hopper and a flow regulator, then into a mold.

7.9.2 Emissions and Controls

The principal pollutants emitted from secondary copper smelting activities are particulate matter in various forms. Removal of insulation from wire by burning causes particulate emissions of metal oxides and unburned insulation. Drying of chips and borings to remove excess oils and cutting fluids can cause discharges of large amounts of dense smoke consisting of soot and unburned hydrocarbons. Particulate emissions from the top of a cupola furnace consist of metal oxide fumes, dirt, and dust from limestone and coke.

The smelting process utilizes large volumes of air to oxidize sulfides, zinc, and other undesirable constituents of the feed. This procedure generates much particulate matter in the exit gas stream. The wide variation among furnace types, charge types, quality, extent of pretreatment, and size of charge is reflected in a broad spectrum of particle sizes and variable grain loadings in the escaping gases. One major factor contributing to differences in emission rates is the amount of zinc present in scrap feed materials; the low-boiling zinc evaporates and combines with air oxygen to give copious fumes of zinc oxide.

Metal oxide fumes from furnaces used in secondary smelters have been controlled by baghouses, electrostatic precipitators, or wet scrubbers. Efficiency of control by baghouses may be better than 99 percent, but cooling systems are needed to prevent the hot exhaust gases from damaging or destroying the bag filters. A two-stage system employing both water jacketing and radiant cooling is common. Electrostatic precipitators are not as well suited to this application, having a low collection efficiency for dense particulates such as oxides of lead and zinc. Wet scrubber installations are also relatively ineffective in the secondary copper industry. Scrubbers are useful mainly for particles larger than 1 micron, but the metal oxide fumes generated are generally submicron in size.

Particulate emissions associated with drying kilns can be similarly controlled. Drying temperatures up to 150°C (300°F) produce relatively cool exhaust gases, requiring no precooling for control by baghouses.

Wire burning generates much particulate matter, largely unburned combustibles. These emissions can be effectively controlled by direct-flame afterburners, with an efficiency of 90 percent or better if the afterburner combustion temperature is maintained above 1,000°C (1,800°F). If the insulation contains chlorinated organics such as polyvinyl chloride, hydrogen chloride gas will be generated and will not be controlled by the afterburner.

One source of fugitive emissions in secondary smelter operations is charging of scrap into furnaces containing molten metals. This often occurs when the scrap being processed is not sufficiently compact to allow a full charge to fit into the furnace prior to heating. The introduction of additional material onto the liquid metal surface produces significant amounts of volatile and combustible materials and smoke which can escape through the charging

door. Briquetting the charge offers a possible means of avoiding the necessity of such fractional charges. When fractional charging cannot be eliminated, fugitive emissions are reduced by turning off the furnace burners during charging. This reduces the flow of exhaust gases and enhances the ability of the exhaust control system to handle the emissions.

Metal oxide fumes are generated not only during melting, but also during pouring of the molten metal into the molds. Other dusts may be generated by the charcoal, or other lining, used in association with the mold. Covering the metal surface with ground charcoal is a method used to make "smooth-top" ingots. This process creates a shower of sparks, releasing emissions into the plant environment at the vicinity of the furnace top and the molds being filled.

Emission factor averages and ranges for six different types of furnaces are presented in Table 7.9-1.

Table 7.9-1. EMISSION FACTORS FOR PARTICULATE MATTER AND ALLOYING FROM FURNACES USED IN SECONDARY COPPER SMELTING AND ALLOYING PROCESSES[a]

A. Cupolas

Type of charge	Control[b] equipment	Emissions				No. of units tested	No. of plants tested
		Avg (kg/MT)	Range (kg/MT)	Avg (lb/ton)	Range (lb/ton)		
Scrap copper	0	0.002	-	0.003	-	1	1
Insulated copper wire	0	120	-	230	-	1	1
Insulated copper wire	1	5	-	10	-		1
Scrap copper and brass	0	35	30-40	70	60-80	2	1
Scrap copper and brass	1	1.2	1.0-1.4	2.4	2.0-2.8	2	1

B. Reverberatory Furnaces

Type of charge	Control[b] equipment	Emissions				No. of units tested	No. of plants tested
		Avg (kg/MT)	Range (kg/MT)	Avg (lb/ton)	Range (lb/ton)		
Copper	0	2.6	0.4-15	5.1	0.8-30		12
Copper	2	0.2	0.1-0.3	0.4	0.3-0.6	2	2
Brass and bronze	0	18	0.3-35	36	0.6-70	2	2
Brass and bronze	2	1.3	0.3-2.5	2.6	0.05-5	2	2

[a]All factors given in terms of raw materials charged to unit.

[b]Control equipment: 0 signifies none operated
1 indicates electrostatic precipitator used
2 indicates baghouse filter system

Table 7.9-1. EMISSION FACTORS FOR PARTICULATE MATTER AND ALLOYING FROM FURNACES USED IN SECONDARY COPPER SMELTING AND ALLOYING PROCESSES (CONTINUED)[a]

C. Rotary Furnaces

Type of charge	Control[b] equipment	Emissions				No. of units tested	No. of plants tested
		Avg (kg/MT)	Range (kg/MT)	Avg (lb/ton)	Range (lb/ton)		
Brass and bronze	0	150	50-250	300	100-500	2	2
	1	7	3-10	13	6-19	3	3

D. Crucible and Pot Furnaces

Type of charge	Control[b] equipment	Emissions				No. of units tested	No. of plants tested
		Avg (kg/MT)	Range (kg/MT)	Avg (lb/ton)	Range (lb/ton)		
Brass and bronze	0	11	1-20	21	2-40	17	13
	1	0.5	0.1-1	1	0.1-2	5	3

[a]All factors given in terms of raw materials charged to unit.

[b]Control equipment: 0 signifies none operated
1 indicates electrostatic precipitator used
2 indicates baghouse filter system

Table 7.9-1. EMISSION FACTORS FOR PARTICULATE MATTER AND ALLOYING FROM FURNACES USED IN SECONDARY COPPER SMELTING AND ALLOYING PROCESSES (CONCLUDED)[a]

E. Electric Arc Furnaces

Type of charge	Control[b] equipment	Emissions				No. of units tested	No. of plants tested
		Avg (kg/MT)	Range (kg/MT)	Avg (lb/ton)	Range (lb/ton)		
Copper	0	2.5	1-4	5	2-8	3	2
	2	0.5	0.02-1.0	1	0.04-2	2	1
Brass and bronze	0	5.5	2-9	11	4-18		2
	2	3	-	6	-	1	1

F. Electric Induction Furnaces

Type of charge	Control[b] equipment	Emissions				No. of units tested	No. of plants tested
		Avg (kg/MT)	Range (kg/MT)	Avg (lb/ton)	Range (lb/ton)		
Copper	0	3.5	-	7	-	1	1
	2	0.25	-	0.5	-	1	1
Brass and bronze	0	10	0.3-20	20	0.5-40	-	18
	2	0.35	0.01-0.65	0.7	0.01-1.3	-	6

[a]All factors given in terms of raw materials charged to unit.

[b]Control equipment: 0 signifies none operated
1 indicates electrostatic precipitator used
2 indicates baghouse filter system

Additional footnotes to Table 7.9-1.

[b]The information for Table 7.9-1 was based on unpublished data furnished by the following:

Philadelphia Air Management Services, Philadelphia, Pennsylvania

New Jersey Department of Environmental Protection, Trenton, New Jersey

New Jersey Department of Environmental Protection, Metro field office, Springfield, New Jersey

New Jersey Department of Environmental Protection, Newark field office, Newark, New Jersey

New York State Department of Environmental Conservation, New York, New York

The City of New York Department of Air Resources, New York, New York

Cook County Department of Environmental Control, Maywood, Illinois

Wayne County Department of Health, Air Pollution Control Division, Detroit, Michigan

City of Cleveland Department of Public Health and Welfare, Division of Air Pollution Control, Cleveland, Ohio

State of Ohio Environmental Protection Agency, Columbus, Ohio

City of Chicago Department of Environmental Control, Chicago, Illinois

South Coast Air Quality Management District, Los Angeles, California

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16. ABSTRACT

This document describes procedures and methodology used to obtain information necessary to upgrade emission factors in the primary and secondary copper smelting industries. Engineering management information on operational characteristics of process equipment in these industries is included, to the extent relevant to derivation or application of emission factors. Related information regarding alloying and casting has been included, as well as information about emissions from similar furnaces used in nonferrous foundry operations. Appendices include sections submitted for inclusion in EPA Publication AP-42 and Process Compendia for both industries.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Air Pollution Emissions: sulfur dioxide, particulates, metallic oxides. Primary copper smelters. Secondary copper smelters. Alloying. Casting. Emission factors: smelters, converters, furnaces.	Upgrading emission factors. Operational characteristics of process equipment. Process compendia	Air Pollution

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