

## 12.9 Secondary Copper Smelting

### 12.9.1 General<sup>1,2</sup>

As of 1992, more than 40 percent of the U. S. supply of copper is derived from secondary sources, including such items as machine shop punchings, turnings, and borings; manufacturing facility defective or surplus goods; automobile radiators, pipes, wires, bushings, and bearings; and metallurgical process skimmings and dross. This secondary copper can be refined into relatively pure metallic copper, alloyed with zinc or tin to form brass or bronze, incorporated into chemical products, or used in a number of smaller applications. Six secondary copper smelters are in operation in the U. S.: 3 in Illinois and 1 each in Georgia, Pennsylvania, and South Carolina. A large number of mills and foundries reclaim relatively pure copper scrap for alloying purposes.

### 12.9.2 Process Description<sup>2,3</sup>

Secondary copper recovery is divided into 4 separate operations: scrap pretreatment, smelting, alloying, and casting. Pretreatment includes the cleaning and consolidation of scrap in preparation for smelting. Smelting consists of heating and treating the scrap for separation and purification of specific metals. Alloying involves the addition of 1 or more other metals to copper to obtain desirable qualities characteristic of the combination of metals. The major secondary copper smelting operations are shown in Figure 12.9-1; brass and bronze alloying operations are shown in Figure 12.9-2.

#### 12.9.2.1 Pretreatment -

Scrap pretreatment may be achieved through manual, mechanical, pyrometallurgical, or hydrometallurgical methods. Manual and mechanical methods include sorting, stripping, shredding, and magnetic separation. The scrap may then be compressed into briquettes in a hydraulic press. Pyrometallurgical pretreatment may include sweating (the separation of different metals by slowly staging furnace air temperatures to liquify each metal separately), burning insulation from copper wire, and drying in rotary kilns to volatilize oil and other organic compounds. Hydrometallurgical pretreatment methods include flotation and leaching to recover copper from slag. Flotation is typically used when slag contains greater than 10 percent copper. The slag is slowly cooled such that large, relatively pure crystals are formed and recovered. The remaining slag is cooled, ground, and combined with water and chemicals that facilitate flotation. Compressed air and the flotation chemicals separate the ground slag into various fractions of minerals. Additives cause the copper to float in a foam of air bubbles for subsequent removal, dewatering, and concentration.

Leaching is used to recover copper from slime, a byproduct of electrolytic refining. In this process, sulfuric acid is circulated through the slime in a pressure filter. Copper dissolves in the acid to form a solution of copper sulfate ( $\text{CuSO}_4$ ), which can then be either mixed with the electrolyte in the refinery cells or sold as a product.

#### 12.9.2.2 Smelting -

Smelting of low-grade copper scrap begins with melting in either a blast or a rotary furnace, resulting in slag and impure copper. If a blast furnace is used, this copper is charged to a converter, where the purity is increased to about 80 to 90 percent, and then to a reverberatory furnace, where copper of about 99 percent purity is achieved. In these fire-refining furnaces, flux is added to the copper and air is blown upward through the mixture to oxidize impurities. These impurities are then

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LEAVING THE SYSTEM

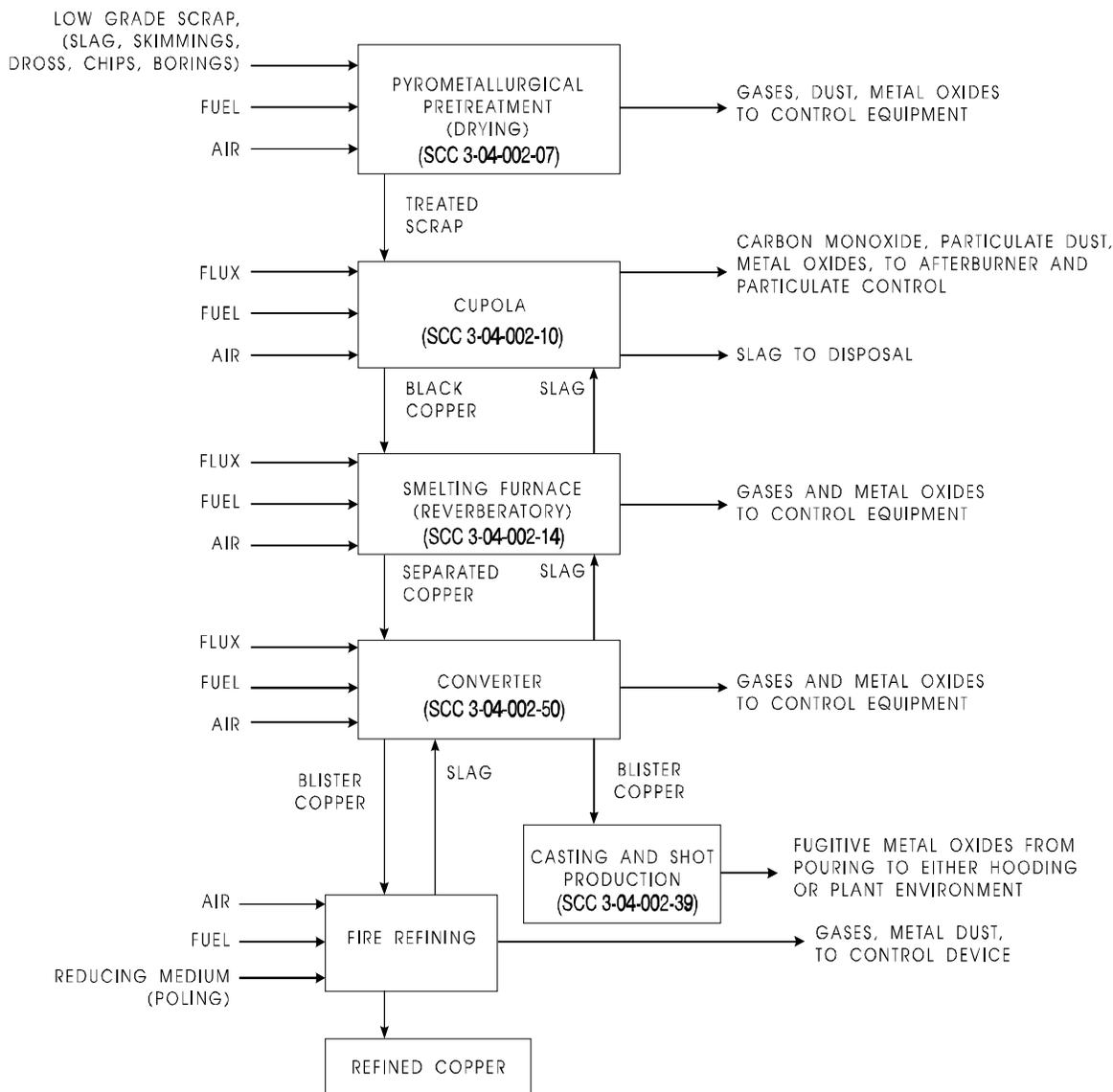


Figure 12.9-1. Low-grade copper recovery.  
(Source Classification Codes in parentheses.)

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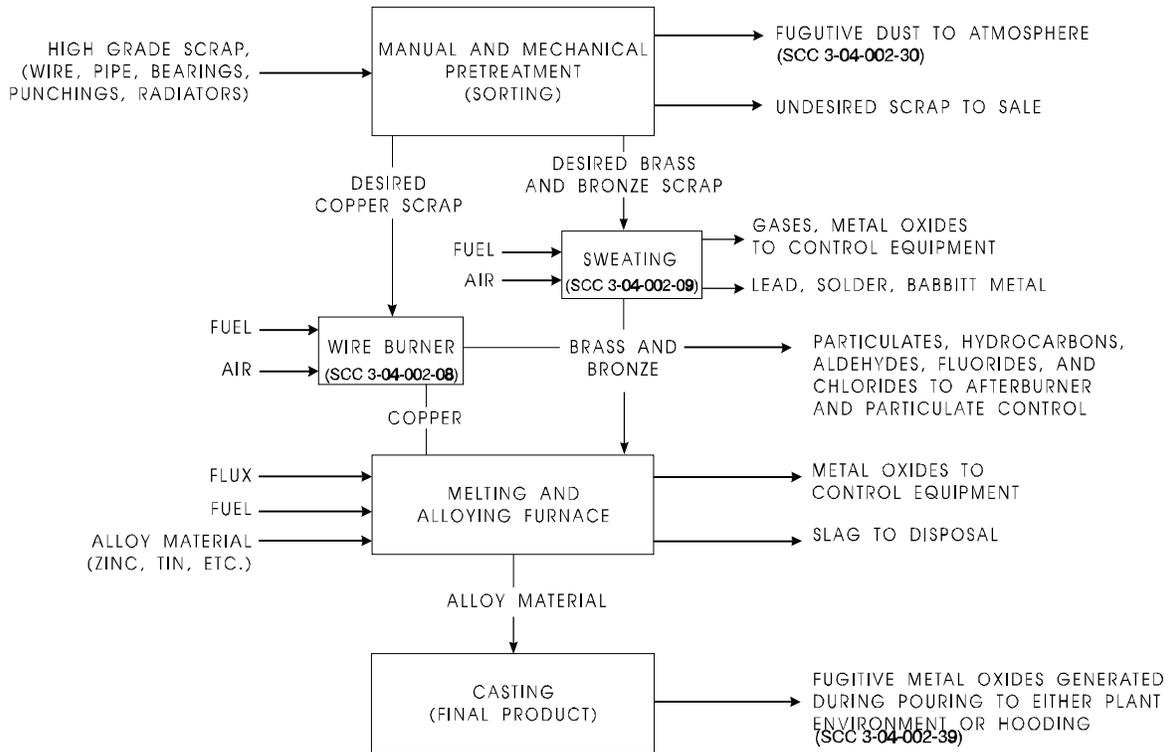


Figure 12.9-2. High-grade brass and bronze alloying.  
(Source Classification Codes in parentheses.)

removed as slag. Then, by reducing the furnace atmosphere, cuprous oxide (CuO) is converted to copper. Fire-refined copper is cast into anodes, which are used during electrolysis. The anodes are submerged in a sulfuric acid solution containing copper sulfate. As copper is dissolved from the anodes, it deposits on the cathode. Then the cathode copper, which is as much as 99.99 percent pure, is extracted and recast. The blast furnace and converter may be omitted from the process if average copper content of the scrap being used is greater than about 90 percent.

The process used by 1 U. S. facility involves the use of a patented top-blown rotary converter in lieu of the blast, converting, and reverberatory furnaces and the electrolytic refining process described above. This facility begins with low-grade copper scrap and conducts its entire refining operation in a single vessel.

### 12.9.2.3 Alloying -

In alloying, copper-containing scrap is charged to a melting furnace along with 1 or more other metals such as tin, zinc, silver, lead, aluminum, or nickel. Fluxes are added to remove impurities and to protect the melt against oxidation by air. Air or pure oxygen may be blown through the melt to

adjust the composition by oxidizing excess zinc. The alloying process is, to some extent, mutually exclusive of the smelting and refining processes described above that lead to relatively pure copper.

#### 12.9.2.4 Casting -

The final recovery process step is the casting of alloyed or refined metal products. The molten metal is poured into molds from ladles or small pots serving as surge hoppers and flow regulators. The resulting products include shot, wirebar, anodes, cathodes, ingots, or other cast shapes.

### 12.9.3 Emissions And Controls<sup>3</sup>

The principal pollutant emitted from secondary copper smelting activities is particulate matter. As is characteristic of secondary metallurgical industries, pyrometallurgical processes used to separate or refine the desired metal, such as the burning of insulation from copper wire, result in emissions of metal oxides and unburned insulation. Similarly, drying of chips and borings to remove excess oils and cutting fluids can cause discharges of volatile organic compounds (VOC) and products of incomplete combustion.

The smelting process utilizes large volumes of air to oxidize sulfides, zinc, and other undesirable constituents of the scrap. This oxidation procedure generates particulate matter in the exhaust gas stream. A broad spectrum of particle sizes and grain loadings exists in the escaping gases due to variations in furnace design and in the quality of furnace charges. Another major factor contributing to differences in emission rates is the amount of zinc present in scrap feed materials. The low-boiling zinc volatilizes and is oxidized to produce copious amounts of zinc oxide as submicron particulate.

Fabric filter baghouses are the most effective control technology applied to secondary copper smelters. The control efficiency of these baghouses may exceed 99 percent, but cooling systems may be needed to prevent hot exhaust gases from damaging or destroying the bag filters. Electrostatic precipitators are not as well suited to this application, because they have a low collection efficiency for dense particulate such as oxides of lead and zinc. Wet scrubber installations are ineffective as pollution control devices in the secondary copper industry because scrubbers are useful for particles larger than 1 micrometer ( $\mu\text{m}$ ), and the metal oxide fumes generated are generally submicron in size.

Particulate emissions associated with drying kilns can also be controlled with baghouses. Drying temperatures up to 150°C (300°F) produce exhaust gases that require no precooling prior to the baghouse inlet. Wire burning generates large amounts of particulate matter, primarily composed of partially combusted organic compounds. These emissions can be effectively controlled by direct-flame incinerators called afterburners. An efficiency of 90 percent or more can be achieved if the afterburner combustion temperature is maintained above 1000°C (1800°F). If the insulation contains chlorinated organics such as polyvinyl chloride, hydrogen chloride gas will be generated. Hydrogen chloride is not controlled by the afterburner and is emitted to the atmosphere.

Fugitive emissions occur from each process associated with secondary copper smelter operations. These emissions occur during the pretreating of scrap, the charging of scrap into furnaces containing molten metals, the transfer of molten copper from one operation to another, and from material handling. When charging scrap into furnaces, fugitive emissions often occur when the scrap 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. If this smoke exceeds the capacity of the exiting capture devices and control equipment, it can escape through the charging door. Forming scrap bricquettes offers a possible means of avoiding the necessity of fractional charges. When fractional

charging cannot be eliminated, fugitive emissions are reduced by turning off the furnace burners during charging. This reduces the flow rate of exhaust gases and allows the exhaust control system to better accommodate the additional temporary emissions.

Fugitive emissions of metal oxide fumes are generated not only during melting, but also while pouring molten metal into molds. Additional dusts may be generated by the charcoal or other lining used in the mold. The method used to make "smooth-top" ingots involves covering the metal surface with ground charcoal. 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.

The electrolytic refining process produces emissions of sulfuric acid mist, but no data quantifying these emissions are available.

Emission factor averages and ranges for 6 different types of furnaces are presented in Tables 12.9-1 and 12.9-2, along with PM-10 emission rates and reported fugitive and lead emissions. Several of the metals contained in much of the scrap used in secondary copper smelting operations, particularly lead, nickel, and cadmium, are hazardous air pollutants (HAPs) as defined in Title III of the 1990 Clean Air Act Amendments. These metals will exist in the particulate matter emitted from these processes in proportions related to their existence in the scrap.

Table 12.9-1 (Metric Units). PARTICULATE EMISSION FACTORS FOR FURNACES USED IN SECONDARY COPPER SMELTING AND ALLOYING PROCESS<sup>a</sup>

Furnace And Charge Type	Control Equipment	Total Particulate	EMISSION FACTOR RATING	PM-10 <sup>b</sup>	EMISSION FACTOR RATING	Lead <sup>c</sup>	EMISSION FACTOR RATING
<b>Cupola</b>							
Scrap iron (SCC 3-04-002-13)	None	0.002	B	ND	NA	ND	NA
Insulated copper wire (SCC 3-04-002-11)	None ESP <sup>d</sup>	120 5	B B	105.6 ND	E NA	ND ND	NA NA
Scrap copper and brass (SCC 3-04-002-12)	None ESP <sup>d</sup>	35 1.2	B B	32.1 ND	E NA	ND ND	NA NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-34)	None	ND	NA	1.1	E	ND	NA
<b>Reverberatory furnace</b>							
High lead alloy (58%) (SCC 3-04-002-43)	None	ND	NA	ND	NA	25	B
Red/yellow brass (SCC 3-04-002-44)	None	ND	NA	ND	NA	6.6	B
Other alloy (7%) (SCC 3-04-002-42)	None	ND	NA	ND	NA	2.5	B
Copper (SCC 3-04-002-14)	None	2.6	B	2.5	E	ND	NA
Brass and bronze (SCC 3-04-002-15)	Baghouse	0.2	B	ND	NA	ND	NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-35)	None	18	B	10.8	E	ND	NA
	Baghouse	1.3	B	ND	NA	ND	NA
	None	ND	NA	1.5	E	ND	NA
<b>Rotary furnace</b>							
Brass and bronze (SCC 3-04-002-17)	None ESP <sup>d</sup>	150 7	B B	88.3 ND	E NA	ND ND	NA NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-36)	None	ND	NA	1.3	E	ND	NA
<b>Crucible and pot furnace</b>							
Brass and bronze (SCC 3-04-002-19)	None ESP <sup>d</sup>	11 0.5	B B	6.2 ND	E NA	ND ND	NA NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-37)	None	ND	NA	0.14	E	ND	NA
<b>Electric arc furnace</b>							
Copper (SCC 3-04-002-20)	None Baghouse	2.5 0.5	B B	2.5 ND	E NA	ND ND	NA NA
Brass and bronze (SCC 3-04-002-21)	None Baghouse	5.5 3	B B	3.2 ND	E NA	ND ND	NA NA
<b>Electric induction</b>							
Copper (SCC 3-04-002-23)	None Baghouse	3.5 0.25	B B	3.5 ND	E NA	ND ND	NA NA
Brass and bronze (SCC 3-04-002-24)	None Baghouse	10 0.35	B B	10 ND	E NA	ND ND	NA NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-38)	None	ND	NA	0.04	E	ND	NA

Table 12.9-1 (cont.).

- <sup>a</sup> Expressed as kg of pollutant/Mg ore processed. The information for particulate in Table 12.9-1 was based on unpublished data furnished by the following:
- Philadelphia Air Management Services, Philadelphia, PA.
  - New Jersey Department of Environmental Protection, Trenton, NJ.
  - New Jersey Department of Environmental Protection, Metro Field Office, Springfield, NJ.
  - New Jersey Department of Environmental Protection, Newark Field Office, Newark, NJ.
  - New York State Department of Environmental Conservation, New York, NY.
  - The City of New York Department of Air Resources, New York, NY.
  - Cook County Department of Environmental Control, Maywood, IL.
  - Wayne County Department of Health, Air Pollution Division, Detroit, MI.
  - City of Cleveland Department of Public Health and Welfare, Division of Air Pollution Control, Cleveland, OH.
  - State of Ohio Environmental Protection Agency, Columbus, OH.
  - City of Chicago Department of Environmental Control, Chicago, IL.
  - South Coast Air Quality Management District, Los Angeles, CA.
- <sup>b</sup> PM-10 and fugitive emissions are listed in *Airs Facility Subsystem Source Classification Codes and Emission Factor Listing for Criteria Air Pollutants*, U.S Environmental Protection Agency, EPA 450/4-90-003, March 1990. These estimates should be considered to have an emission factor rating of E.
- <sup>c</sup> References 1,6-7. Expressed as kg of pollutant/Mg product.
- <sup>d</sup> ESP = electrostatic precipitator.

Table 12.9-2 (English Units). PARTICULATE EMISSION FACTORS FOR FURNACES USED IN SECONDARY COPPER SMELTING AND ALLOYING PROCESS<sup>a</sup>

Furnace And Charge Type	Control Equipment	Total Particulate	EMISSION FACTOR RATING	PM-10 <sup>b</sup>	EMISSION FACTOR RATING	Lead <sup>c</sup>	EMISSION FACTOR RATING
<b>Cupola</b>							
Scrap iron (SCC 3-04-002-13)	None	0.003	B	ND	NA	ND	NA
Insulated copper wire (SCC 3-04-002-11)	None ESP <sup>d</sup>	230 10	B B	211.6 ND	E NA	ND ND	NA NA
Scrap copper and brass (SCC 3-04-002-12)	None ESP <sup>d</sup>	70 2.4	B	64.4 ND	E NA	ND ND	NA NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-34)	None	ND	NA	2.2	E	ND	NA
<b>Reverberatory furnace</b>							
High lead alloy (58%) (SCC 3-04-002-43)	None	ND	NA	ND	NA	50	B
Red/yellow brass (SCC 3-04-002-44)	None	ND	NA	ND	NA	13.2	B
Other alloy (7%) (SCC 3-04-002-42)	None	ND	NA	ND	NA	5.0	B
Copper (SCC 3-04-002-14)	None Baghouse	5.1 0.4	B B	5.1 ND	E NA	ND ND	NA NA
Brass and bronze (SCC 3-04-002-15)	None Baghouse	36 2.6	B B	21.2 ND	E NA	ND ND	NA NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-35)	None	ND	NA	3.1	E	ND	NA
<b>Rotary furnace</b>							
Brass and bronze (SCC 3-04-002-17)	None ESP <sup>d</sup>	300 13	B B	177.0 ND	E NA	ND ND	NA NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-36)	None	ND	NA	2.6	E	ND	NA
<b>Crucible and pot furnace</b>							
Brass and bronze (SCC 3-04-002-19)	None ESP <sup>d</sup>	21 1	B B	12.4 ND	E NA	ND ND	NA NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-37)	None	ND	NA	0.29	E	ND	NA
<b>Electric arc furnace</b>							
Copper (SCC 3-04-002-20)	None Baghouse	5 1	B B	5 ND	E NA	ND ND	NA NA
Brass and bronze (SCC 3-04-002-21)	None Baghouse	11 6	B B	6.5 ND	E NA	ND ND	NA NA
<b>Electric induction furnace</b>							
Copper (SCC 3-04-002-23)	None Baghouse	7 0.5	B B	7 ND	E NA	ND ND	NA NA
Brass and bronze (SCC 3-04-002-24)	None Baghouse	20 0.7	B B	20 ND	E NA	ND ND	NA NA
Fugitive emissions <sup>b</sup> (SCC 3-04-002-38)	None	ND	NA	0.04	E	ND	NA

Table 12.9-2 (cont.).

- <sup>a</sup> Expressed as lb of pollutant/ton ore processed. The information for particulate in Table 12.9-2 was based on unpublished data furnished by the following:  
Philadelphia Air Management Services, Philadelphia, PA.  
New Jersey Department of Environmental Protection, Trenton, NJ.  
New Jersey Department of Environmental Protection, Metro Field Office, Springfield, NJ.  
New Jersey Department of Environmental Protection, Newark Field Office, Newark, NJ.  
New York State Department of Environmental Conservation, New York, NY.  
The City of New York Department of Air Resources, New York, NY.  
Cook County Department of Environmental Control, Maywood, IL.  
Wayne County Department of Health, Air Pollution Division, Detroit, MI.  
City of Cleveland Department of Public Health and Welfare, Division of Air Pollution Control, Cleveland, OH.  
State of Ohio Environmental Protection Agency, Columbus, OH.  
City of Chicago Department of Environmental Control, Chicago, IL.  
South Coast Air Quality Management District, Los Angeles, CA.
- <sup>b</sup> PM-10 and fugitive emissions are listed in *Airs Facility Subsystem Source Classification Codes and Emission Factor Listing for Criteria Air Pollutants*, U.S Environmental Protection Agency, EPA 450/4-90-003, March 1990. These estimates should be considered to have an emission factor rating of E.
- <sup>c</sup> References 1,6-7. Expressed as lb of pollutant/ton product.
- <sup>d</sup> ESP = electrostatic precipitator.

References For Section 12.9

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4. *Emission Factors And Emission Source Information For Primary And Secondary Copper Smelters*, U. S. Environmental Protection Agency, Research Triangle Park, NC, Publication No. EPA-450/3-051, December 1977.
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