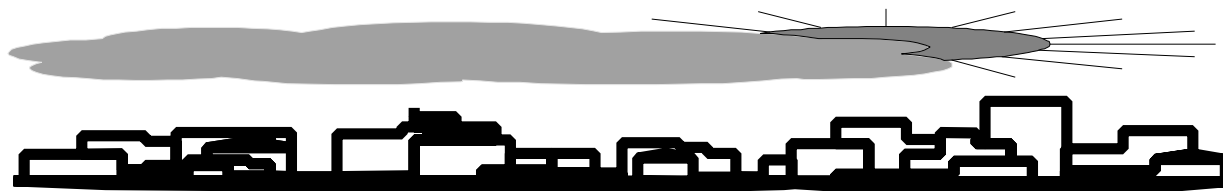


AIR

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# LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF POLYCYCLIC ORGANIC MATTER



# L & E

This report has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and has been approved for publication. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

EPA-454/R-98-014

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## EXECUTIVE SUMMARY

The 1990 Clean Air Act Amendments contain a list of 188 hazardous air pollutants (HAPs) which the U.S. Environmental Protection Agency must study, identify sources of, and determine if regulations are warranted. One of these HAPs, polycyclic organic matter (POM), is the subject of this document. This document describes the properties of POM as an air pollutant, how it is formed, identifies source categories of air emissions, and provides POM emissions data in terms of emission factors. This document is part of an ongoing EPA series designed to assist the general public at large, but primarily State/local air agencies, in identifying sources of HAPs and determining emissions estimates.

The principal formation mechanism for POM occurs as part of the fuel combustion process present in many different types of source categories. A secondary formation mechanism is the volatilization of light-weight POM compounds. The combustion processes are much more significant in terms of overall POM air emissions, and include sources such as stationary external combustion for heat and electricity generation, internal combustion engines and turbines, motor vehicles, and a variety of fuel combustion processes in the industrial sector.

The term POM defines not one compound, but a broad class of compounds which generally includes all organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 212°F (100°C). Theoretically, millions of POM compounds could be formed. However, only a small portion of these compounds have actually been identified and regularly tested for as part of emissions tests.

Sixteen polycyclic aromatic hydrocarbons (PAHs), a subset of the class of POM compounds, were designated by EPA as compounds of interest under a suggested procedure for reporting test measurement results.<sup>1</sup> The PAHs included in this measurement procedure are:

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<sup>1</sup> U.S. Environmental Protection Agency. Second Supplement to Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina. EPA-600/4-89-018. pp. TO-13 to TO-97. 1988.

Naphthalene	Benzo(ghi)perylene
Acenaphthene	Benzo(a)anthracene*
Acenaphthylene	Chrysene*
Fluorene	Benzo(b)fluoranthene*
Phenanthrene	Benzo(k)fluoranthene*
Anthracene	Benzo(a)pyrene*
Fluoranthene	Dibenz(a,h)anthracene*
Pyrene	Indeno(1,2,3-cd)pyrene*

The pollutants with asterisks (\*) correspond to a subset of seven PAHs that have been identified by the International Agency for Research on Cancer (IARC) as animal carcinogens and have been studied by the EPA as potential human carcinogens.<sup>2</sup>

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<sup>2</sup> U.S. Environmental Protection Agency. Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons. Office of Research and Development, Washington, DC. EPA-600/R-93-089. July 1993.

SECTION 1.0  
PURPOSE OF DOCUMENT

The U.S. Environmental Protection Agency (EPA), State, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, limited information is available on the ambient air concentrations of these substances or about the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of locating and estimating (L&E) documents such as this one that compiles available information on sources and emissions of these substances. Other documents in the series are listed below:

<u>Substance or Source Category</u>	<u>EPA Publication Number</u>
Acrylonitrile	EPA-450/4-84-007a
Arsenic	EPA-454/R-98-013
Benzene	EPA-454/R-98-011
1,3-Butadiene	EPA-454/R-96-008
Cadmium	EPA-454/R-93-040
Carbon Tetrachloride	EPA-450/4-84-007b
Chlorobenzenes (revised)	EPA-454/R-93-044
Chloroform	EPA-450/4-84-007c
Chromium	EPA-450/4-84-007g
Chromium (supplement)	EPA-450/2-89-002
Coal and Oil Combustion Sources	EPA-450/2-89-001
Cyanide Compounds	EPA-454/R-93-041
Epichlorohydrin	EPA-450/4-84-007j
Ethylene Oxide	EPA-450/4-84-007i

<u>Substance or Source Category</u>	<u>EPA Publication Number</u>
Ethylene Dichloride	EPA-450/4-84-007d
Formaldehyde	EPA-450/2-91-012
Lead	EPA-454/R-98-006
Manganese	EPA-450/4-84-007h
Medical Waste Incinerators	EPA-454/R-93-053
Mercury and Mercury Compounds	EPA-453/R-93-023
Methyl Chloroform	EPA-454/R-93-045
Methyl Ethyl Ketone	EPA-454/R-93-046
Methylene Chloride	EPA-454/R-93-006
Municipal Waste Combustors	EPA-450/2-89-006
Nickel	EPA-450/4-84-007f
Organic Liquid Storage Tanks	EPA-450/4-88-004
Perchloroethylene and Trichloroethylene	EPA-450/2-90-013
Phosgene	EPA-450/4-84-007i
Polychlorinated Biphenyls (PCB)	EPA-450/4-84-007n
Sewage Sludge Incineration	EPA-450/2-90-009
Styrene	EPA-454/R-93-011
Toluene	EPA-454/R-93-047
Vinylidene Chloride	EPA-450/4-84-007k
Xylenes	EPA-454/R-93-048

This document deals specifically with polycyclic organic matter (POM). Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of POM and estimating their air emissions.

Because of the limited availability of data on potential sources of POM emissions and the variability in process configurations, control equipment, and operating procedure among facilities, this document is best used as a primer on (1) types of sources that may emit POM, (2) process variations and release points that may be expected, and (3) available emissions information on the potential for POM releases into the air. The reader is cautioned against using

the emissions information in this document to develop an exact assessment of emissions from any particular facility. Because of the limited background data available, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This document represents an update to a previous L&E document for POM that was published by the EPA in 1987. Since that time there has been new research and testing associated with some of the source categories that were previously identified. Also, new source categories emitting POM have been identified and some source categories discussed in the previous document are no longer in existence. For this update, an effort was made to obtain more up-to-date information from an extensive literature search. The search was limited to the years 1986 to the present and to items in the English language.

Databases searched include the following:

- Factor Information Retrieval System (FIRE) - which contains emission factors and other information for a variety of source categories;
- CASEARCH - which contains information on chemistry and applications literature;
- INSPEC - A database of physics, electronics, and computer abstracts;
- NTIS - which contains information on government-sponsored research, development, engineering, and analysis activities;
- COMPENDEX PLUS - A database of literature from the engineering sciences; and
- APILIT - A database maintained by the American Petroleum Institute, containing information on activities related to the petroleum industry.

The literature search identified several hundred potential references or citations. These citations were journal articles, handbooks and texts, Federal and State documents, and

conference papers. The list of titles and abstracts from the literature search were reviewed to identify: (1) new information for known source categories, (2) additional source categories, and (3) test data for categories that were not otherwise well characterized.

Another potential source of emissions data for POM is the Toxic Chemical Release Inventory (TRI) reporting data required by Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA 313). SARA 313 requires owners and operators of certain facilities that manufacture, import, process, or otherwise use certain toxic chemicals to report annually their releases of these chemicals to any environmental media. As part of SARA 313, EPA provides public access to the annual emissions data.

The reader is cautioned that TRI will not likely provide facility, emissions, and chemical release data sufficient for conducting detailed exposure modeling and risk assessment. In many cases, the TRI data are based on annual estimates of emissions (i.e., on emission factors, material balance calculations, and engineering judgment). Also, TRI includes only a limited number of POM compounds; there are many more POM compounds that are emitted to the air and which are included in this document. We recommend the use of TRI data in conjunction with the information provided in this document to locate potential emitters of POM and to make preliminary estimates of air emissions from these facilities.

As standard procedure, L&E documents are sent to government, industry, and environmental groups for review wherever EPA is aware of expertise. These groups are given the opportunity to review the document, comment on its contents, and provide additional data where applicable. Where necessary, the document is then revised to incorporate these comments. Although this document has undergone extensive review, there may still be shortcomings. Comments subsequent to publication are welcome and will be addressed based on available time and resources. In addition, any information on process descriptions, operating parameters,



control measures, and emissions information that would enable EPA to improve on the contents of this document is welcome. Comments and information may be sent to the following address:

Group Leader  
Emission Factor and Inventory Group (MD-14)  
Office of Air Quality Planning and Standards  
U. S. Environmental Protection Agency  
Research Triangle Park, North Carolina 27711

## SECTION 2.0 OVERVIEW OF DOCUMENT CONTENTS

This section provides an overview of the contents of this document. It briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3.0 of this document provides a brief summary of the physical and chemical characteristics of POM, its basic formation mechanisms, and its potential transformations in ambient air. This background section may be useful to someone who needs to develop a general perspective on the nature of POM, how it is defined, and how it is formed in the combustion process.

Section 4.0 of this document focuses on major sources of POM air emissions. Stationary, mobile, and natural sources of POM air emissions are discussed. For each air emission source category described in Section 4.0, the following subsections are discussed: (1) a general process description, including emissions control techniques, (2) emission factor development, and (3) source location. Flow diagrams are provided for most of the industry-based categories, identifying potential points of emissions. The emission factor subsections provide a discussion of available data for each source category and present the emission factors in tabular format. For certain source categories, emission factor data were not available; in these cases only a process description and source location discussion are provided. Within the source location subsections, the names and locations of all major stationary source facilities known to be operating and potentially emitting POM are presented (for industries having 100 or less facilities). For area sources of POM emissions with distinct national distributions, and industries with over 100 facilities, geographic areas where such activities primarily occur are identified.

Section 5.0 describes evaporative emission sources from the production and use of naphthalene, which is a specific POM compound. Naphthalene is one of the lighter weight POM compounds that can be emitted through volatilization. The source categories described in

Section 5.0 involve the direct production and use of naphthalene, which is commercially produced and widely consumed.

Section 6.0 of this document summarizes available procedures for source sampling and analysis of POM. The summaries provide an overview of applicable sampling procedures and cites references for those interested in conducting source tests.

Appendix A provides a summary of emission factors used by the EPA in developing national emission estimates for POM as part of the supporting data to develop a national strategy to control POM emissions under Section 112(c)(6) of the Clean Air Act (CAA). Section 3.2 of this document provides information on the development of the emission factors in Appendix A.

Each emission factor listed in Sections 4.0 and 5.0 was assigned an emission factor rating (A, B, C, D, E, or U) based on the criteria for assigning data quality ratings and emission factor ratings as required in the document Procedures for Preparing Emission Factor Documents (U.S. EPA, 1997). The criteria for assigning the data quality ratings are as follows:

- A - Tests are performed by using an EPA reference test method, or when not applicable, a sound methodology. Tests are reported in enough detail for adequate validation, and raw data are provided that can be used to duplicate the emission results presented in the report.
- B - Tests are performed by a generally sound methodology, but lacked enough detail for adequate validation. Data are insufficient to completely duplicate the emission result presented in the report.
- C - Tests are based on an unproven or new methodology, or are lacking a significant amount of background information.
- D - Tests was based on a generally unacceptable method, but the method may provide an order-of-magnitude value for the source.

Once the data quality ratings for the source tests had been assigned, these ratings along with the number of source tests available for a given emission point were evaluated. Because of the almost impossible task of assigning a meaningful confidence limit to

industry-specific variables (e.g., sample size versus sample population, industry and facility variability, method of measurement), the use of a statistical confidence interval for establishing a representative emission factor for each source category was not practical. Therefore, some subjective quality rating was necessary. The following emission factor quality ratings were used in the emission factor tables in this document:

- A - Excellent. Emission factor is developed primarily from A- and B-rated source test data taken from many randomly chosen facilities in the industry population. The source category population is sufficiently specific to minimize variability.
- B - Above average. Emission factor is developed primarily from A- or B-rated test data from a moderate number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.
- C - Average. Emission factor is developed primarily from A-, B-, and C-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.
- D - Below average. Emission factor is developed primarily from A-, B-, and C-rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source population.
- E - Poor. Factor is developed from C- rated and D-rated test data from a very few number of facilities, and there may be reasons to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population.
- U - Unrated (Only used in the L&E documents). Emission factor is developed from source tests which have not been thoroughly evaluated, research papers, modeling data, or other sources that may lack supporting documentation. The data are not necessarily “poor,” but there is not enough information to rate the factors according to the rating protocol.

This document does not contain any discussion of health or other environmental effects of POM, nor does it include any discussion of ambient air levels.

## SECTION 2.0 REFERENCES

U.S. Environmental Protection Agency. Procedures for Preparing Emission Factor Documents. Research Triangle, North Carolina. EPA-454/R-95-015. November 1997.

## SECTION 3.0 BACKGROUND

### 3.1 NATURE OF POLLUTANT

The term polycyclic organic matter (POM) defines a broad class of compounds which generally includes all organic structures having two or more fused aromatic rings (i.e., rings which share a common border). Further definition is provided in Section 112(b)(1) of the 1990 Clean Air Act Amendments (CAAA), where POM is listed as a hazardous air pollutant (HAP) with a footnote stating that it includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 212°F (100°C). Polycyclic organic matter has been identified with up to seven fused rings and, theoretically, millions of POM compounds could be formed; however, only about 100 species have been identified and studied and typically only a small fraction of these are regularly tested for as part of emissions measurement programs (U.S. EPA, 1980). Any effort to quantify emissions of POM relies on the group of compounds or analytes targeted by the test method employed.

Eight major categories of compounds have been defined by the EPA to constitute the class known as POM (U.S. EPA, 1975; Lahre, 1987). The categories are as follows:

1. Polycyclic aromatic hydrocarbons (PAHs) - the PAHs include naphthalene, phenanthrene, anthracene, fluoranthene, acenaphthalene, chrysene, benz(a)anthracene, cyclopenta(cd)pyrene, the benzpyrenes, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene, coronene, and some of the alkyl derivatives of these compounds. PAHs are also known as polynuclear aromatics (PNAs).
2. Aza arenes - aromatic hydrocarbons containing nitrogen in a heterocyclic ring.
3. Imino arenes - aromatic hydrocarbons containing a carbon-nitrogen double bond (C=NH).
4. Carbonyl arenes - aromatic hydrocarbons containing a one ring carbonyl divalent group (C=O).

5. Dicarbonyl arenes - also known as quinones; contain two ring carbonyl divalent groups.
6. Hydroxy carbonyl arenes - carbonyl arenes containing hydroxy groups and possibly alkoxy or acyloxy groups.
7. Oxa arenes and thia arenes - oxa arenes are aromatic hydrocarbons containing an oxygen atom in a heterocyclic ring; thia arenes are aromatic hydrocarbons containing a sulfur atom in a heterocyclic ring.
8. Polyhalo compounds - some polyhalo compounds, such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), may be considered as POM although they do not have two or more fused aromatic rings.

These categories were developed to better define and standardize the types of compounds considered to be POM.

The POM chemical groups most commonly tested for and reported in emission source exhaust and ambient air are PAHs, which contain carbon and hydrogen only. Information available in the literature and from emissions testing on POM compounds generally pertains to PAHs. Because of the dominance of PAH information (as opposed to other POM categories) in the literature, many reference sources have inaccurately used the terms POM and PAH interchangeably. By definition, all PAH compounds can be classified as POM but not all POM compounds can be defined as PAHs. This issue becomes important when comparing POM inventory and emissions data from different references sources where the term “POM” is not explicitly defined. In these cases POM could represent two entirely different sets of compounds, and therefore would not be suitable for direct comparison.

### 3.2 FORMAT OF POM DATA FOR THE DOCUMENT

In order to avoid the historical problems of using a singular “POM” listing for emission factor data and information, the emission factor tables presented in Sections 4.0 and 5.0 of this report show individual POM compounds, most of which could be classified as PAH. This

allows for a direct calculation of emissions for a known compound. The discussions accompanying each table will generally refer to “POM” compounds when describing processes or operations that affect the class of compounds as a whole. However, where the information is specific to PAHs, the discussion utilizes the “PAH” terminology.

The following list of 16 PAHs were designated by EPA as compounds of interest under a suggested procedure for reporting test measurement results (U.S. EPA, 1988). The 16 PAHs included in this measurement procedure are:

Naphthalene	Benzo(ghi)perylene
Acenaphthene	Benzo(a)anthracene*
Acenaphthylene	Chrysene*
Fluorene	Benzo(b)fluoranthene*
Phenanthrene	Benzo(k)fluoranthene*
Anthracene	Benzo(a)pyrene*
Fluoranthene	Dibenz(a,h)anthracene*
Pyrene	Indeno(1,2,3-cd)pyrene*

These 16 compounds are routinely detected and reported from source tests as they are target analytes in standard EPA and State sampling and analytical methods. The pollutants with asterisks (\*) correspond to the subset of seven PAHs. These seven PAHs have been identified by the International Agency for Research on Cancer (IARC) as animal carcinogens and have been studied by the EPA as potential human carcinogens (U.S. EPA, 1993).

The emission factor tables in Sections 4.0 and 5.0 first list all of the 7-PAH compounds. The rest of the 16-PAH group of compounds are listed next. Other POM compounds that are not part of the 16-PAH subset are listed at the end of each table. For some source categories, there were not individual PAH emission factors for all 16 PAHs in the subset; therefore, the list of compounds varies from source to source in some cases. However, in all cases, the order of pollutants begins with compounds from the 7-PAH subset; followed by the



remaining compounds from the 16-PAH grouping, and finally, any other POM compounds for which emission factor data were found.

Appendix A provides a summary of 7-PAH and 16-PAH emission factors for source categories for which the EPA has developed national emission estimates to meet the requirements of Section 112 (c)(6) of the CAAA. Section 112 (c)(6) requires the EPA to look at seven specific pollutants, including POM, in order to develop a national strategy to control these pollutants. The source categories listed in Appendix A do not represent all the potential POM source categories discussed in this document. The EPA did not always have activity levels to match to the available emission factors for every source category, so Appendix A only contains those categories for which an activity level was available to calculate national emissions.

The 7-PAH and 16-PAH emission factors in Appendix A are presented as the sum of the individual POM compounds making up the 16-PAH and 7-PAH subsets as described above. For most of the source categories listed in Appendix A, the 16-PAH and 7-PAH emission factors were derived from the individual POM compound emission factors presented in the emission factor tables in this document. The exceptions are the “Ferroalloy Manufacturing” and the “Onroad Vehicles” source categories; the 16-PAH and 7-PAH emission factors contained in Appendix A for these source categories were developed by EPA specifically for the purpose of the national emission inventory efforts and were not derived from the emission factor tables contained in this document for those categories. The 16-PAH and 7-PAH emission factors for these categories were developed by EPA from alternative sources for which background information on the individual POM compounds included in the 16-PAH and 7-PAH subsets was not available to present in a consistent format with this document (i.e., individual POM species factors were not available). When using the emission factors in Appendix A, the user should keep in mind that these were developed to be representative of nationwide activity and do not, in many cases, represent the particularities of a specific site. If modeling specific site conditions, or if the focus is on individual POM compounds, the user should refer to the emission factor tables for the particular source category contained in this document.

Because POM is not one compound but potentially several thousand, it is not reasonable to describe the properties and characteristics of all POM compounds. Instead, general background information is provided for the primary POM compounds, such as PAHs, that are known to exist in ambient air. Considerably more detailed data on POM chemical and physical properties exist than are presented in this document. The prevalent, more useful information is presented here to provide an understanding of the basic nature of POM compounds and emissions. The references cited at the end of each section contain useful information and should be consulted when further detail is required.

### 3.3 NOMENCLATURE AND STRUCTURE OF SELECTED POMs

In the past, the nomenclature of POM compounds has not been standardized and ambiguities have existed due to different peripheral numbering systems. The currently accepted nomenclature is that adopted by the International Union of Pure and Applied Chemistry (IUPAC) and by the Chemical Abstracts Service Registry (National Academy of Sciences, 1972). The following rules help determine the orientation from which the numbering is assigned:

1. The maximum number of rings lie in a horizontal row;
2. As many rings as possible are above and to the right of the horizontal row; and
3. If more than one orientation meets these requirements, the one with the minimum number of rings at the lower left is chosen (Loening and Merrit, 1983).

The carbons are then numbered in a clockwise fashion, starting with the first counterclockwise carbon which is not part of another ring and is not engaged in a ring fusion. Letters are assigned in alphabetical order to faces of rings, beginning with “a” for the side between carbon atoms 1 and 2 and continuing clockwise around the molecule. Ring faces common to two rings are not lettered. The molecular structures of the more predominantly identified and studied POM compounds (mainly PAHs) are shown in Figure 3-1.

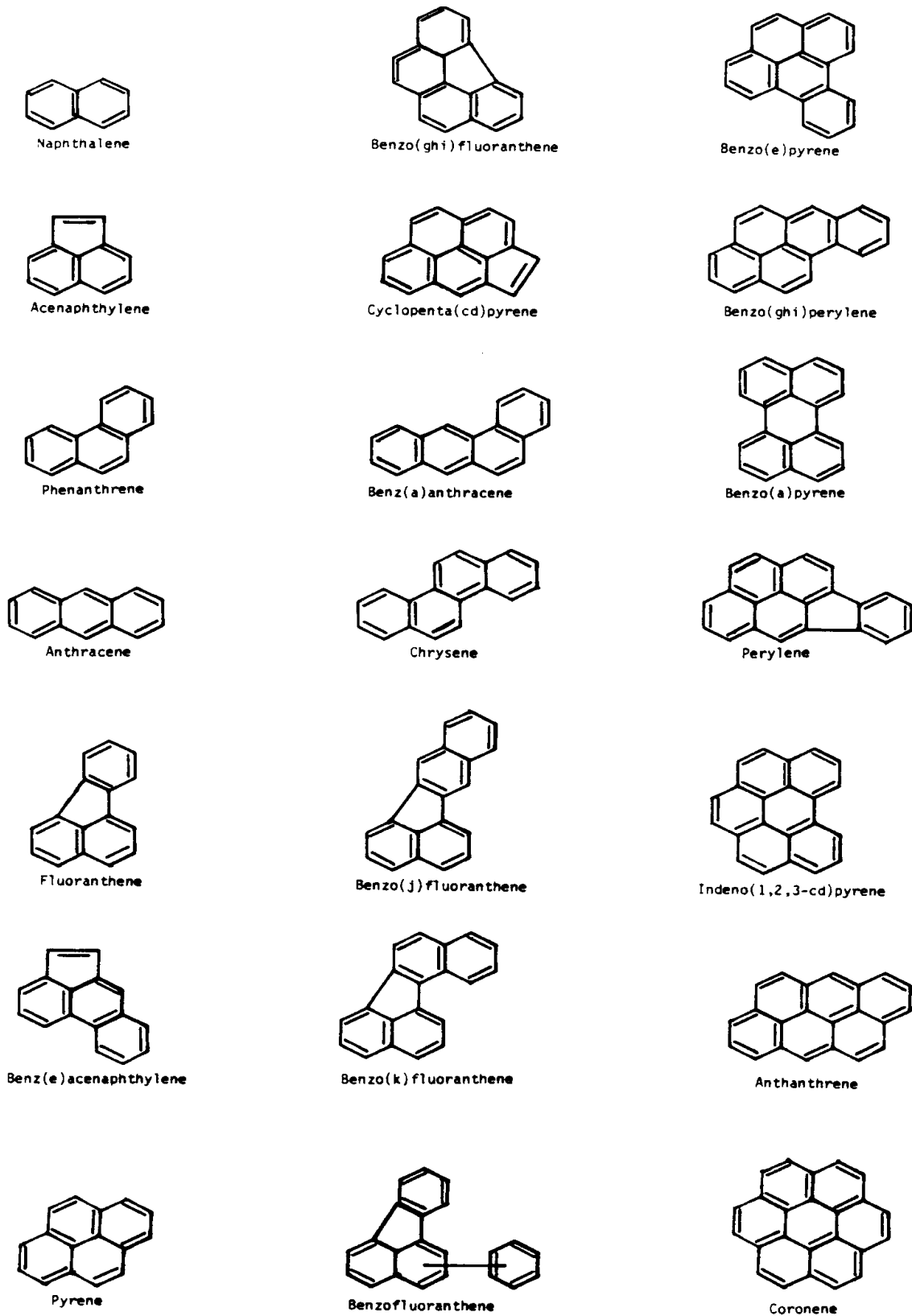


Figure 3-1. Structures of Selected Polycyclic Aromatic Organic Molecules

Source: U.S. EPA, 1978.

### 3.4 PHYSICAL PROPERTIES OF POM

Most POM compounds are solids with high melting and boiling points and are extremely insoluble in water. The PAHs are primarily planar, nonpolar compounds with melting points considerably over 212°F (100°C). Phenanthrene, with a melting point of 214°F (101°C) and benzo(c)phenanthrene, with a melting point of 154°F (68°C) are two exceptions. The molecular weights, melting points, and boiling points of selected POM species are listed in Table 3-1.

The vapor pressures of POM compounds vary depending upon the ring size and the molecular weight of each species. The vapor pressure of pure compounds varies from  $6.8 \times 10^{-4}$  mmHg for phenanthrene (3 rings and 14 carbons) to  $1.5 \times 10^{-12}$  mmHg for coronene (7 rings and 24 carbons) (U.S. EPA, 1978). A POM compound's vapor pressure has considerable impact on the amount of POM that is adsorbed onto particulate matter in the atmosphere and retained on particulate matter during collection of air sampling and during laboratory handling. Retention of POM species on particulates during collection and handling also depends upon temperature, velocity of the air stream during collection, properties of the particulate matter, and the adsorption characteristic of the individual POMs. Table 3-1 includes vapor pressures at 86°F (30°C) for selected POMs.

The ultraviolet absorption spectra are available for many POM compounds. Most of the polycyclic aromatic hydrocarbons absorb light at wavelengths found in sunlight (>300 nm) and are believed to be photochemically reactive by direct excitation. The available spectra data reflect characteristics of PAHs in organic solvents; however, PAHs in the environment are usually particulate-bound and as such may have considerably different absorption properties.

TABLE 3-1. PHYSICAL PROPERTIES OF VARIOUS POM COMPOUNDS

Compound	Chemical Formula	Molecular Weight	Melting Point °F (°C)	Boiling Point <sup>a</sup> °F (°C)	Vapor Pressure <sup>b</sup> (mmHg)
Napthalene	C <sub>10</sub> H <sub>8</sub>	128.19	177 (80.5)	424 (218)	NR <sup>c</sup>
Acenaphthene	C <sub>12</sub> H <sub>10</sub>	154.21	187 (96.2)	534 (279)	NR
Fluorene	C <sub>13</sub> H <sub>10</sub>	166.22	241-243 (116 - 117)	563 (295)	NR
Anthracene	C <sub>14</sub> H <sub>10</sub>	178.24	422-423 (216.5 - 217.2)	644 (339.9)	1.95 x 10 <sup>-4</sup>
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	178.24	212-214 (100 - 101)	644 (340)	6.8 x 10 <sup>-4</sup>
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	202.26	231-232 (110.6 - 111.0)	739 (393)	NR
Pyrene	C <sub>16</sub> H <sub>10</sub>	202.26	306-307 (152.2 - 152.9)	680 (360)	6.85 x 10 <sup>-7</sup>
Benz(a)anthracene	C <sub>18</sub> H <sub>12</sub>	228.30	319-321 (159.5 - 160.5)	815 (435)	1.1 x 10 <sup>-7</sup>
Chrysene	C <sub>18</sub> H <sub>12</sub>	228.30	482-489 (250 - 254)	838 (448)	NR
Benzo(a)pyrene	C <sub>20</sub> H <sub>12</sub>	252.32	350-352 (176.5 - 177.5)	592 (311)	5.5 x 10 <sup>-9</sup>
Benzo(k)fluoranthene	C <sub>20</sub> H <sub>12</sub>	252.32	420-421 (215.5 - 216)	NR	9.6 x 10 <sup>-11</sup>
Perylene	C <sub>20</sub> H <sub>12</sub>	252.32	523-525 (273 - 274)	932 (500)	NR
Benzo(ghi)perylene	C <sub>22</sub> H <sub>12</sub>	276.33	523 (273)	NR	1.01 x 10 <sup>-10</sup>
Dibenz(a,h)anthracene	C <sub>22</sub> H <sub>14</sub>	278.36	401 (205)	NR	NR
Coronene	C <sub>24</sub> H <sub>12</sub>	300.36	820 (438)	977 (525)	1.47 x 10 <sup>-12</sup>

<sup>a</sup>Each boiling point is at a pressure of 1 atm, except the boiling point of benzo(a)pyrene is at a pressure of 10 mmHg.

<sup>b</sup>All vapor pressures are at 86°F (30°C).

<sup>c</sup>NR means data not reported.

Sources: U.S. EPA, 1980; Tucker, 1979; U.S. EPA, 1978; CRC, 1983.

### 3.5 CHEMICAL PROPERTIES OF POM

The chemistry of POMs is quite complex and differs from one compound to another. Most of the information available in the literature concerns the polycyclic aromatic hydrocarbons. Generally, the PAHs are more reactive than benzene and the reactivities toward methyl radicals tend to increase with greater conjugation. Conjugated rings are structures which have double bonds that alternate with single bonds. Conjugated compounds are generally more stable but, toward free radical addition, they are more reactive (Morrison and Boyd, 1978). For example, in comparison to benzene, naphthalene and benz(a)anthracene, which have greater conjugation, react with methyl radicals 22 and 468 times faster, respectively.

The PAHs undergo electrophilic substitution reactions quite readily. An electrophilic reagent attaches to the ring to form an intermediate carbonium ion; to restore the stable aromatic system, the carbonium ion then gives up a proton. Oxidation and reduction reactions occur to the stage where a substituted benzene ring is formed. Rates of electrophilic, nucleophilic, and free radical substitution reactions are typically greater for the PAHs than for benzene.

Environmental factors also influence the reactivity of PAHs. Temperature, light, oxygen, ozone, other chemical agents, catalysts, and the surface areas of particulates that the PAHs are adsorbed onto may play a key role in the chemical reactivity of PAHs.

### 3.6 POM FORMATION

The principle formation mechanism for POM occurs as part of the combustion process present in many different types of sources. A secondary formation mechanism, primarily represented by the naphthalene production and use categories (see Section 5.0 of this document), is the volatilization of light-weight POM compounds. However, the combustion mechanism is much more significant when looking at overall POM formation, and it also much more complex. The following discussion focuses on the combustion mechanism for POM formation.

### 3.6.1 POM from Combustion Processes

POM formation occurs as a result of combustion of carbonaceous material under reducing conditions. The detailed mechanisms are not well understood; however, it is widely accepted that POM is formed via a free radical mechanism which occurs in the gas phase (Natusch et al., 1978). As a result, POM originates as a vapor. There is also overwhelming evidence that POM is present in the atmosphere predominantly in particulate form (Thomas et al., 1968). Therefore, a vapor to particle conversion must take place between the points of formation of POM in the combustion source and its entry to the atmosphere.

It has been recognized that soot (a product of coal combustion) is similar in some structural characteristics to polycyclic aromatic molecules and that both soot and POM are products of combustion (Electric Power Research Institute [EPRI], 1978). Comparisons of the two types of molecules give rise to the first clue as to how POM may be formed in combustion, namely by incomplete combustion and degradation of large fuel molecules such as coal. It is also known, however, that carbon black and soot are produced by burning methane ( $\text{CH}_4$ ). Thus, it is believed that POMs are not only produced by degrading large fuel molecules, but are also produced by polymerizing small organic fragments in rich gaseous hydrocarbon flames. Before examining POM formation per se, it is instructive to first examine carbon (soot) formation in combustion. The two are similar phenomena and a closer examination of some of the earlier studies on soot formation is helpful in understanding POM formation and behavior.

Soot produced in a flame takes on a number of specific characteristics. Soot or carbon particles may be hard and brittle, soft and fatty, brown to black, and contain anywhere from almost 0 to 50 percent hydrogen (based on number of atoms). Generally, it is observed that flame-produced soot is a fluffy, soft material made up of single, almost spherical particles which stick together. Soot properties appear to be independent of the fuel burned in a homogeneous gas flame. However, if hydrocarbon gases (such as methane, propane, or benzene) are passed down a hot tube, the carbon product is quite different from the flame-produced soot. The heterogeneous products are hard, long crystals that are shiny and vitreous.

Carbon-producing flames have been identified and labeled as either the acetylenic type or the benzene type. The acetylenic type flame is one in which carbon, as observed in  $C_2$ -radiation, is emitted from all parts of the flame. Carbon compounds produced in low molecular weight hydrocarbon flames is made up of benzene and other aromatics (benzene type). Instead of  $C_2$ -radiation being emitted from all parts of the flame, a carbon streak is observed that is emitted from the tip of the flame. The basis for the two flame types is related to differences in diffusion properties between the fuel molecule and oxygen. Where the fuel and oxygen are of about the same molecular weight, carbon is observed uniformly in the flame front; where the two differ substantially, enriched pockets of fuel and oxygen occur, and one observes the carbon streak. Thus, the nature of the soot molecule may be independent of the fuel molecule, but its formation is quite dependent on the nature of the fuel and on the method of combustion.

Over the past 25 years, procedures have been developed for analyzing the microstructure and detailed kinetics of processes occurring in flames. A number of investigators have been applying these techniques to studying POM formation in gaseous hydrocarbon flames (Howard and Longwell, 1983; Toqan et al., 1983). In one procedure, a pre-mixed hydrocarbon-air flame is stabilized on a burner (usually as a flat flame) and reactants and products are removed with the aid of a microprobe and analyzed by electron microscope or other techniques.

Changes in the molecular weight of POM products as they pass through the flame have been documented. Just above the flame, a large number of POM products are observed, while farther downstream the number of products is considerably reduced. Based on this observation, it appears that a large number of reactive POM products are produced just past the flame zone. These POMs are referred to as reactive POMs, in that they contain many organic side chains ( $CH_2$ ,  $C_2H_5$ , etc.) attached to the rings of the basic POM structures. The reactive POMs, however, degrade in the hot region of the flames so that further downstream only the more stable condensed ring structures are observed.

The changes in POM structure noted above are corroborated in other studies. It has been shown that with time a steady increase occurs in the production of lower molecular



weight POMs (e.g., anthracene, phenanthrene, fluoranthene, and pyrene), while the higher molecular weight POMs such as benzopyrene, benzoperylene, and coronene reach a maximum and then decline in concentration with increasing distance from the flame. Studies by Toqan et al. (1983) show that soot is formed in the region of the flame where a sharp decline of POM compound is observed. They conclude that the POM (particularly PAH) compounds are precursors to soot formation. From the preceding discussion, it is apparent that POM may be a precursor as well as a byproduct of soot formation.

The question of how the polyacetylenes (that are produced by a sequence of rapid reaction steps) cyclize still remains. One theory is that the polyacetylene chain bends around the carbon atoms and eventually bonds into the condensed ring structures. Another plausible hypothesis is illustrated in Figure 3-2. The association shown requires minimum atomic rearrangements. Also, the formation of polyacetylene cyclics is highly exothermic, thereby providing sufficient energy to dissociate terminal groups and the free valences to produce reactive and stable POMs.

Pyrolytic studies of aromatic and straight chain hydrocarbons have been conducted which offer logical mechanisms for explaining POM formation (Crittenden and Long, 1976). An example explaining the formation of fluoranthene, phenanthrene, and benzo(a)pyrene is shown in Figure 3-3. In this instance, the example illustrates how phenyl-, butadienyl-, and phenyl butadienyl radicals produced in the pyrolysis of phenylbutadiene may react with naphthalene to produce the three POM products.

In conclusion, there is no single, dominant mechanism for POM formation in flames. In rich gas flames, polyacetylenes can be built up via a  $C_2H$  polymerization mechanism. In coal and oil droplet flames, pyrolytic degradation mechanisms prevail. In either instance, soot and POM are related and persist in post-rich flames due to a deficiency of hydroxide radicals.

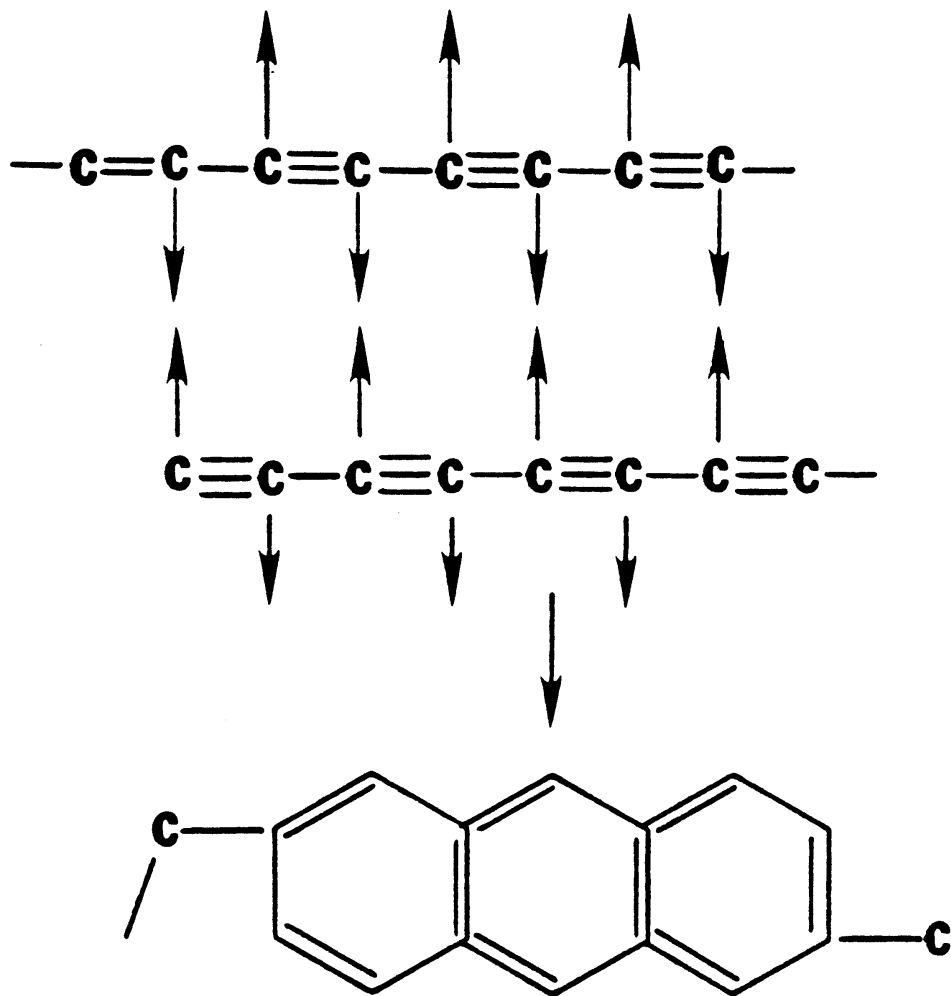


Figure 3-2. Hypothesized Ring Closure

Source: EPRI, December 1978.

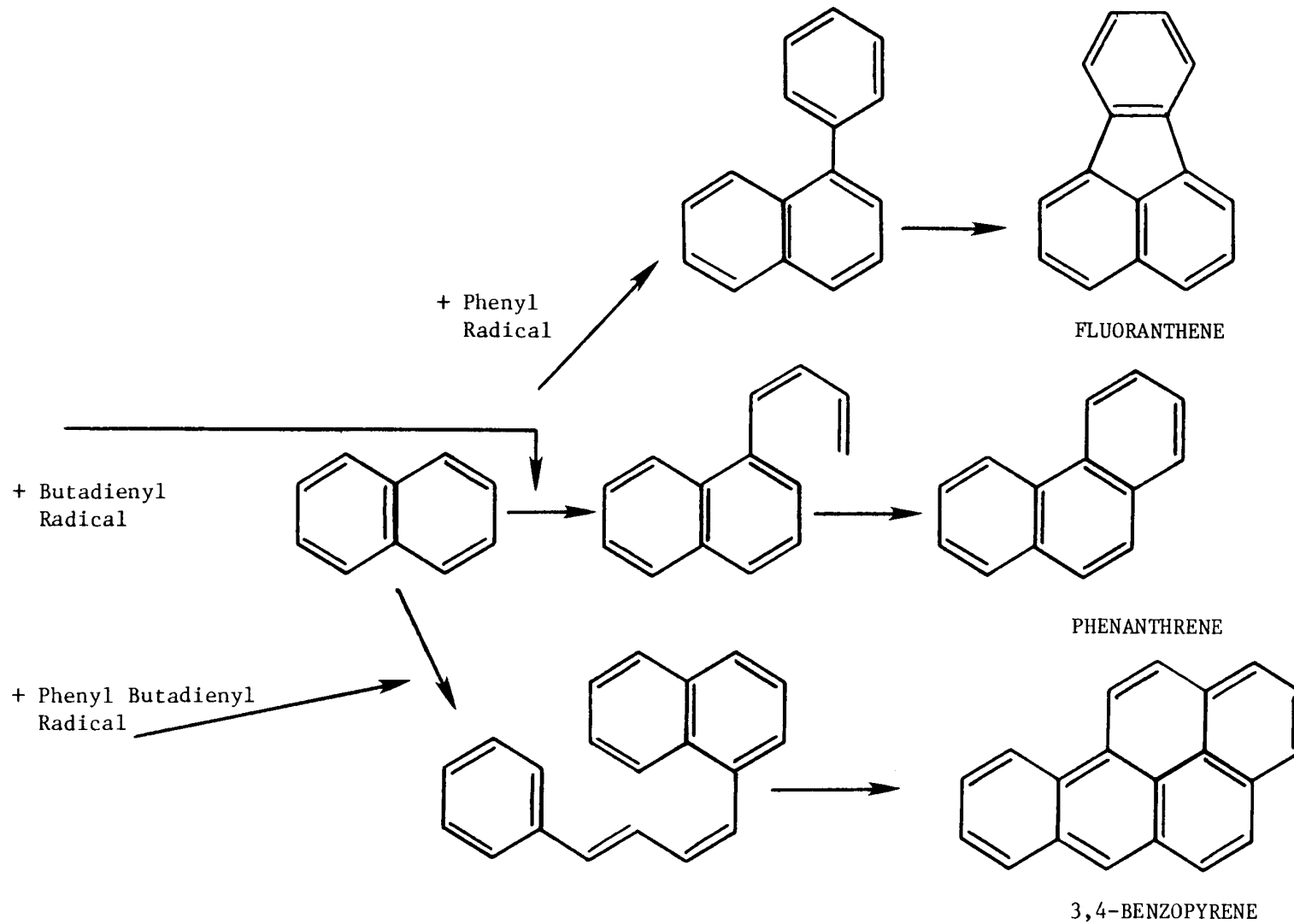


Figure 3-3. POM Formation by Pyrolysis

### 3.6.2 Conversion of POM from Vapor to Particulate

Polycyclic organic matter formed during combustion is thought to exist primarily in the vapor phase at the temperatures encountered near the flame. However, POM encountered in the ambient atmosphere is almost exclusively in the form of particulate material (Schure et al., 1982). It is thought that the vapor phase material formed initially becomes associated with particles by adsorption as the gas stream cools or possibly by condensation and subsequent nucleation (Schure et al., 1982; National Academy of Sciences, 1983). The lack of open-channel porosity, the large concentration of oxygen functional groups on the surface of particulates such as soot, and the adherence of airborne benzo(a)pyrene to the particle in a manner that allows for ready extraction indicate that benzo(a)pyrene and presumably other POM compounds are primarily adsorbed on the surface of particulates through hydrogen bonding.

The physical state of POM in ambient air is determined in part by the amount of particulate generated by the source. Natusch and Tomkins contend that the extent of POM adsorption onto particulate is proportional to the frequency of collision of POM molecules with available surface area, resulting in preferential enrichment of smaller diameter particulates (Natusch and Tomkins, 1978). In areas of high particulate concentrations, such as the stack of a fossil fuel power plant, one would expect nearly complete adsorption of the POM onto particulates. As particulate concentration decreases, as in internal combustion engines, one would expect to find more POM in the condensed phase. In general, the largest concentration of POM per unit of particulate mass will be found in the smaller diameter aerosol particulates. Natusch has developed a detailed mathematical model describing the adsorption and condensation mechanisms of POM compounds (Natusch, 1978). The model can describe the temperature dependence of both adsorption and condensation for several different surface behavioral scenarios.

While both adsorption and condensation may be in operation, it appears that the POM vapor pressures encountered in most combustion sources are not high enough for condensation or nucleation to occur (see Table 3-1). The saturation vapor pressure or dew point of POM must be attained for these processes to take place. Conversely, adsorption of POM

vapor onto the surface of particulate material present in stack or exhaust gases can certainly take place and could account for the occurrence of the particulate POM at ambient atmospheric temperatures. Specifically, the modeling exercises conducted by Natusch have shown that:

1. The most important parameters to be considered in an adsorption model are the adsorption energetics, the surface area, and the vapor phase concentration of the adsorbate.
2. Surface heterogeneity will broaden the temperature range where adsorption becomes significant.
3. The particle surface temperature determines the adsorption characteristics. The gas phase temperature is of secondary importance.
4. For conditions found in a typical coal-fired power plant, homogenous condensation is not highly favored since vapor phase levels of POM are, in most cases, below the saturated vapor concentration.
5. The kinetics of adsorption are predicted to be fast, suggesting that an equilibrium model may be adequate for modeling the adsorption behavior of POM (Natusch, 1984).

Field measurement studies have been conducted to investigate the occurrence of vapor to particle conversion in a combustion source (DeAngelis et al., 1979). Measurements were made in the stack system and in the emitted plume of a small coal-fired power plant possessing no particle control equipment. Fly ash samples were collected during the same time periods both inside the stack (temperature at 554°F [290°C]) and from the emitted plume (temperature at 41°F [5°C]). Collected material was extracted and analyzed for POM. Only crude vapor traps were employed during sample collection so no quantitative measure of vapor phase POM was obtained. It was assumed that all POM collected was in the particulate phase. The results of this field test show that considerably more particulate POM is associated with fly ash collected from the plume at a temperature of 41°F (5°C) than from that collected from the same stream at a temperature of 554°F (290°C). Furthermore, since the two collection points were only 100 ft (30.5 m) apart, quite rapid vapor to particle conversion is indicated.

Laboratory studies have been conducted to determine the rate and extent of POM adsorption onto particulate matter. In one study, a stream of air containing pyrene was passed over a bed of fresh coal fly ash which had previously been shown to contain no detectable POM (Sonnichsen, 1983). The objective was to expose all particles to the same concentration of pyrene for different amounts of time and to determine the specific concentrations of adsorbed pyrene as a function of time at different temperatures. The results of this experiment showed that the amount of adsorbed pyrene required to saturate the fly ash increased significantly with decreasing temperature. The rate at which the adsorption process takes place, even at ambient temperatures, is very rapid; on the order of a few seconds. In another study, PAH and soot were sampled from the exhaust gases of a laminar, premixed flat flame under laboratory conditions (Prado et al., 1981). Sampling at different filter temperatures was studied to assess partitioning of PAH between vapor phase and soot. The data shown in Table 3-2 indicate that at low temperatures (104°F [40°C]), the compounds were adsorbed or condensed on the soot particles, while at high temperatures (392°F [200°C]), only the heaviest species were condensed to any significant extent. While these experiments are essentially qualitative, they do establish that coal fly ash and soot will strongly adsorb various POM species, and that the saturation capacity of the adsorbate is inversely related to temperature.

### 3.6.3 Persistence and Fate in the Atmosphere

Polycyclic organic matter emitted as primary pollutants present on particulate matter can be subject to further chemical transformation through gas-particle interactions occurring either in exhaust systems, stacks, emission plumes, or during atmospheric transport. When emitted into polluted urban atmospheres, especially areas with photochemical smog that has a high oxidizing potential, particle-adsorbed PAH are exposed to a variety of gaseous co-pollutants. These include highly reactive intermediates (both free radicals and excited molecular species) and stable molecules. Seasonal variation in transformation reactions of PAH have been observed. During winter, with conditions of low temperature and low irradiation, the major pathway for PAH degradation is probably reactions with nitrogen oxides, sulfur oxides and with the corresponding acids. During summer months, with conditions of high temperatures and intense irradiation, photochemical reactions with oxygen and secondary air pollutants produced

TABLE 3-2. PERCENT OF TOTAL PAH ASSOCIATED WITH SOOT PARTICLES AS A FUNCTION OF TEMPERATURE

Compound	104°F (40°C)	131°F (55°C)	185°F (85°C)	392°F (200°C)
Naphthalene	56	6.5	4.3	0.11
Methylnaphthalene	39	a	20	0.00
Biphenyl	89	77	48	0.46
Biphenylene	88	70	66	0.09
Fluorene	98	94	b	2.1
Phenanthrene and Anthracene	90	92	71	4.6
4H-Cyclopenta-(def)phenanthrene	97	b	85	2.3
Fluoranthene	99	b	82	38
Pyrene and Benzacenaphthylene	99	b	83	33

<sup>a</sup>GC/MS analysis not available.

<sup>b</sup>Interferences from contaminants; accurate values not determined.

Source: Prado et al., 1981.

by photolysis, such as ozone and hydroxyl and hydroperoxyl radicals, are important (Van Cauwenberghe, 1985).

The PAH group of POM compounds in pure solid or solution form undergo different transformation rates than PAH adsorbed onto other substrates. Because atmospheric PAH is predominately found adsorbed onto particulates, transformation mechanisms discussed in this section concentrate on that form. Numerous studies have shown differences in transformation reactions when various PAHs are present as a pure solid, in solution, or adsorbed onto other solid substrates (Natusch et al., 1978; National Academy of Sciences, 1983; Taskar et al., 1985; Yokley et al., 1986).

#### Atmospheric Physics

Because of the high melting and boiling points of materials classified as POM, the bulk of POM is believed to be linked to aerosols in the atmosphere. As POM is mixed with aerosols in the atmosphere, it is spread among particles of widely varied sizes by collision processes. In one study, DeMaio and Corn found that more than 75 percent of the weight of selected polycyclic hydrocarbons was associated with aerosol particles less than  $2.5 \mu\text{m}$  in radius (DeMaio and Corn, 1966). However, Thomas et al. (1968) found that the amount of benzo(a)pyrene per unit weight of soot was constant in the sources tested. A problem in determining the size fractionation of POM-containing aerosols may be due to the sampling methods. Some of the POM may be lost by vaporization from the smaller particles during sample collection. Katz and Pierce observed that the size-mass distribution of PAH-containing particulates varied with collection site. Particulate sampling near vehicular traffic resulted in a group of PAH-particulate compounds in the submicron range, presumably from exhaust, and a second group of large size PAH-particulates ( $>7.0 \mu\text{m}$ ), presumably from roadway reentrainment (Katz and Pierce, 1976). Sampling stations located away from highways resulted in over 70 percent of the PAH-particulate mass associated with particles less than or equal to  $1.0 \mu\text{m}$  in diameter, which is in agreement with earlier studies.



Particles containing POM are dispersed in air and may be transported great distances from their origin by winds. They are eventually removed from the atmosphere by sedimentation or deposition. Removal is enhanced by washout from under rain clouds and by rainout from within clouds (National Academy of Sciences, 1972; Van Noort and Wondergem, 1985). Deposition of large particles by gravitational settling is important, as well as deposition by impaction as air masses flow around obstacles such as rocks, building and vegetation.

Rain clouds play an important role in the removal of POM-laden aerosols from the atmosphere. Aerosols provide centers for nucleation of water droplets in the atmosphere after the air becomes supersaturated with water vapor. Aerosols inside clouds are captured in droplets and rainout occurs. This in-cloud scavenging of particulates is a result of diffusion, interception, and impaction. When precipitation begins to fall from clouds, the droplets sweep out smaller particles and gas-phase POMs during their fall toward the ground. This process, termed washout or below-cloud scavenging, is believed to be significant in removing many pollutants, including POM, from the atmosphere.

The atmospheric half-life (time required for half the material to be removed or destroyed) of POM as a class is estimated to be approximately 100 to 1,000 hours under dry conditions for particulate-bound POM (Esmen and Corn, 1971). Studies of urban aerosols in Pittsburgh, Pennsylvania demonstrated residence times, without precipitation, of from 4 to 40 days for particles less than 1  $\mu\text{m}$  in diameter and 0.4 to 4 days for particles 1 to 10  $\mu\text{m}$  in diameter. Under precipitation conditions, these times are believed to be somewhat shorter. Studies in Brazil found that under prevailing meteorological and atmospheric conditions, half-life times of 3 days for benzo(a)pyrene and 12.4 days for perylene were typical (Miguel, 1983).

Some of the highly reactive POM compounds are degraded in the atmosphere by reactions with oxidants and by photooxidation (Fox and Olive, 1979). Chemical reactivity of different POM species in the atmosphere may lead to shorter half-lives. Chemical reactivity in the presence of sunlight may lead to transition of POM adsorbed on soot to other material in several hours. A number of different types of POM reactions which occur in the atmosphere and which may affect atmospheric persistence are described in the following sections.

## Reactions with Molecular Oxygen

Gas-particle interaction between molecular oxygen and several POMs in the absence of irradiation appears to be very slow. Long range transport of POM has been reported in the Nordic countries. In the absence of, or under irradiation with low-intensity light, little evidence for degradation of adsorbed PAH has been shown. However, substantial evidence has been found for photochemical transformation of POM adsorbed on a variety of solids. The photosensitivity of adsorbed PAH is strongly dependent on the nature of the surface on which the compound is adsorbed. A study by Taskar et al. has shown differences in the reaction of pyrene when adsorbed on carbon, silica, and alumina. The half-lives for the degradation of pyrene adsorbed on the three types of particles were similar when in the presence of light. In the dark, however, the half-life of pyrene was approximately twice as long as in light for both silica-bound pyrene and alumina-bound pyrene, but no difference was observed for carbon-bound pyrene (Taskar et al., 1985).

A study by Inscoe compared the photo modification of 15 different PAHs, deposited on 4 different adsorbents (silica gel, alumina, cellulose, and acetylated cellulose), under exposure to actinic ultraviolet light and room light (Inscoe, 1964). Four of the PAHs did not react under any of the test conditions (chrysene, phenanthrene, picene, and triphenylene). The other 11 PAH compounds underwent pronounced changes when adsorbed on silica gel and alumina. On the less polar substrates of cellulose and acetylated cellulose, transformations of PAHs were observed but were less extensive and developed more slowly.

Other studies have shown that PAHs adsorbed onto coal fly ash are generally stabilized against photochemical oxidation by comparison with the same compounds present in solution, as the pure solid, or adsorbed onto substrates such as alumina or silica gel (Korfmacher et al., 1979; Korfmacher et al., 1980). This effect has been explained by the hypothesis that the energetic adsorption of PAH onto a highly active surface, such as that of coal fly ash or activated carbon, effectively stabilizes PAH against photooxidation which either increases the electronic excitation energy or decreases the lifetime of the excited state.

## Reactions with Ozone

Degradation studies of PAH in solution exposed to ozone may not be relevant to the determination of their half-life on atmospheric particles. Irradiation does not seem to significantly affect the reactivity of PAHs exposed to ozone (Bjorseth and Olufsen, 1983). Studies have shown an inverse relationship between the half-life of benzo(a)pyrene and the measured ambient ozone concentrations (Lane and Katz, 1977). Table 3-3 shows the half-lives of three POM species in simulated daylight subjected to varying concentrations of ozone. It can be seen that as ozone levels increase, the half-lives of each species decrease.

Studies of various PAH compounds adsorbed onto diesel exhaust particulate matter and exposed to ozone have approximated half-lives on the order of 0.5 to 1 hour for most PAHs measured. This high reactivity of PAH toward ozone on a natural carbonaceous matrix is probably related to the large specific surface of diesel soot particles as well as to its high adsorptive capacity for several gaseous compounds. Experiments also indicate significant conversion at lower, nearly ambient ozone levels. Eisenberg et al. have shown that PAHs on particulate surfaces are oxidized by low levels of singlet oxygen generated under environmental conditions (Eisenberg et al., 1985).

## Other Reactions

Two types of free radical processes may be important for particulate organic matter: the gas-particle interactions between hydroxide radicals from the gas phase and particle-associated PAH, or a direct interaction of organic free radicals present at the particle surface. The larger PAHs are extremely sensitive to electrophilic substitution and to oxidation. Nitrogen oxides or dilute nitric acid can either add to, substitute in, or oxidize polycyclic aromatic hydrocarbons. Transformation of some PAHs to nitro-PAH has been observed in experiments using relatively low concentrations of nitrogen dioxide and nitric acid (Pitts et al., 1978; Nielsen, 1984). The reactions appear to be electrophilic, as electron-donating substituents enhance the reactivity and electron-attracting substituents diminish it. Similar reactions of PAH

TABLE 3-3. HALF LIVES IN HOURS OF SELECTED POM IN SIMULATED DAYLIGHT,<sup>a</sup> SUBJECTED TO VARYING CONCENTRATIONS OF ATMOSPHERIC OXIDANTS (OZONE)

Ozone (ppm)	Benzo(k)fluoranthene	Benzo(a)pyrene	Benzo(b)fluoranthene
0.0	14.1	5.3	8.7
0.19	3.9	0.58	4.2
0.70	3.1	0.20	3.6
2.28	0.9	0.08	1.9

<sup>a</sup>Quartzline lamp.

Source: Lane et al., 1977.

with atmospheric sulfur dioxide, sulfur trioxide, and sulfuric acid have also been observed (Tebbens et al., 1966).

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## SECTION 4.0

### POM EMISSION SOURCE CATEGORIES

This section contains the process descriptions, available emission factor data, and source locations for source categories of POM emissions. Many of the source categories discussed in this section emit POM from the fuel combustion process; however, some of the categories have very unique processes due to the fuel type burned or the type of combustion unit used.

There are few emission controls that are dedicated solely to reduce POM emissions, and therefore there are limited data on the effectiveness of control strategies in reducing POM emissions. Where there are known emission control strategies that may affect POM emissions from a source category, these are discussed as part of the process description. Also, in many cases, there are emission factor data provided for both controlled and uncontrolled units that may be used within a source category.

#### 4.1 STATIONARY EXTERNAL COMBUSTION

The combustion of solid, liquid, and gaseous fuels such as coal, lignite, wood, bagasse, fuel oil, and natural gas has been shown through numerous tests to be a source of POM emissions. Polycyclic organic compounds are formed in these sources as products of incomplete combustion. The rates of POM formation and emissions are dependent on both fuel characteristics and combustion process characteristics. Emissions of POM can originate from POM compounds contained in fuels that are released during combustion or from high-temperature transformations of organic compounds in the combustion zone (Shih et al., 1980; National Research Council, 1972; National Research Council, 1983).

An important fuel characteristic that affects POM formation in combustion sources is the carbon-to-hydrogen ratio and the molecular structure of the fuel (Shih et al., 1980). In general, the higher the carbon-to-hydrogen ratio, the greater the probability of POM compound

formation. Holding other combustion variables constant, the tendency for hydrocarbons present in a fuel to form POM compounds is as follows:

aromatics > cycloolefins > olefins > paraffins

Based on both carbon-to-hydrogen ratio and molecular structure considerations, the tendency for the combustion of various fuels to form POM compounds is as follows: (Shih et al., 1980)

coal > lignite > wood > waste oil > residual oil > distillate oil

These general tendencies may not hold true for every scenario because other combustion characteristics, such as equipment operation and maintenance, also affect POM emissions.

The primary combustion process characteristics affecting POM compound formation and emissions are: (Shih et al., 1980; Barrett et al., 1983)

- Combustion zone temperature;
- Residence time in the combustion zones;
- Turbulence or mixing efficiency between air and fuel;
- Air-to-fuel ratio; and
- Fuel feed size.

Concentrations of PAH have been shown to decrease rapidly with increasing temperature (Shih et al., 1980). The degree to which these process variables can be controlled varies from source to source; however, larger combustion sources, such as utilities and industrial boilers, generally have more monitoring devices and mechanisms for adjusting these variables in order to maximize combustion efficiency. Small commercial units and residential sources typically are more variable in their combustion efficiency because the operator is limited by the unit design in making any specific adjustments.

The main cause of incomplete fuel combustion is insufficient mixing of air, fuel, and combustion products. Mixing is a function of operating practices and fuel-firing configuration. Hand- and stoker-fired solid fuel combustion sources generally exhibit very poor air and fuel mixing relative to other types of combustion sources. Liquid fuel units and pulverized solid fuel units provide good air and fuel mixing (Shih et al., 1980; Kelly, 1983; Barrett et al., 1983).

The air-to-fuel ratio present in the combustion environment is important in POM formation because certain quantities of air (i.e., oxygen) are needed to stoichiometrically carry out complete combustion. Air supply is particularly important in systems with poor air and fuel mixing. Combustion environments with a poor air supply will generally have lower combustion temperatures and will not be capable of completely oxidizing all the fuel. Systems that experience frequent startups and shutdowns will also have poor air-to-fuel ratios. Unburned hydrocarbons, many as POM compounds, can exist in such systems and eventually be emitted through the source stack. Generally, stoker and hand-fired solid fuel combustion sources have problems with insufficient air supply and tend to generate relatively large quantities of POM as a result (Shih et al., 1980; Kelly, 1983; Barrett et al., 1983).

In solid and liquid fuel combustion sources, fuel feed size can influence combustion rate and efficiency; therefore, POM compound formation is affected. For liquid fuel oils, a poor initial fuel droplet size distribution is conducive to poor combustion conditions and an enhanced probability of POM formation. In most cases, fuel droplet size distribution is primarily influenced by fuel viscosity. As fuel viscosity increases, the efficiency of atomization decreases and the droplet size distribution shifts to the direction of larger diameters. Therefore, distillate oils are more readily atomized than residual oils and result in finer droplet size distribution. This behavior, combined with the lower carbon-to-hydrogen ratio of distillate oil, means that residual oil sources inherently have a higher probability of POM formation and emissions than distillate oil sources (Shih et al., 1980; Kelly, 1983).

For solid fuels, fuel size affects POM formation by significantly impacting combustion rate. Solid fuel combustion involves a series of repeated steps, each with the

potential to form POM compounds. First, the volatile components near the surface of a fuel particle are burned, followed by burning of the residual solid structure. As fresh, unreacted solid material is exposed, the process is repeated. Thus, the larger the fuel particle, the greater the number of times this sequence is repeated and the longer the residence time required to complete the combustion process. With succeeding repetitions, the greater the probability of incomplete combustion and POM formation. Stoker and hand-fired solid fuel combustion units represent the greatest potential for POM emissions due to fuel size considerations (Shih et al., 1980).

POM can be emitted from fuel combustion sources in both a gaseous and a particulate phase. The compounds are initially formed as gases, but as the flue gas stream cools, a portion of the POM constituents adsorb to solid fly ash particles present in the stream. The rate of adsorption is dependent on temperature and fly ash and POM compound characteristics. At temperatures above 302°F (150°C), most POM compounds are expected to exist primarily in gaseous form. In several types of fuel combustion systems, it has been shown that POM compounds are preferentially adsorbed to smaller (submicron) fly ash particles because of their larger surface area-to-mass ratios. These behavioral characteristics of POM emissions are important in designing and assessing POM emission control systems (Shih et al., 1980; Kelly, 1983; Griest and Guerin, 1979; Sonnichsen, 1983).

The primary stationary combustion sources emitting POM compounds are boilers, furnaces, heaters, stoves, and fireplaces used to generate heat and/or power in the residential, utility, industrial, and commercial use sectors. A description of the combustion sources, typical emission control equipment, and POM emission factors for each of these major use sectors is provided in the sections that follow.

## SECTION 4.1 REFERENCES

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#### 4.1.1 Residential Heating

The residential sector includes furnaces and boilers burning coal, oil, and natural gas; stoves and fireplaces burning wood; and kerosene heaters. All of these units are designed to heat individual homes. Residential combustion sources are generally not equipped with particulate matter (PM) or gaseous pollutant control devices. In coal- and wood-fired sources, stove design and operating practice changes have been made to lower PM, hydrocarbon, and carbon monoxide (CO) emissions. Changes include modified combustion air flow control, better thermal control and heat storage, and the use of combustion catalysts. Such changes can conceivably lead to reduced POM formation and emissions (Mead et al., 1986; Kelly, 1983).

##### Process Description--Residential Wood Combustion

Residential wood combustion generally occurs in either a stove or fireplace unit located inside a house. PAH emissions from wood combustion in residential heating units result from the combination of free radical species formed in the flame zone, primarily as the result of incomplete combustion. These emissions can vary widely depending on how the units are operated and the how the emissions are measured. The following factors will affect PAH emissions measured from residential wood combustion sources (Johnson et al., 1990a):

- Unit design and degree of excess air;
- Wood type, moisture content, and other wood characteristics;
- Burn rate and stage of burn;
- Firebox and chimney temperatures; and
- Sampling and analytical methods.

The following discussions describe the specific characterization of wood-fired stoves (woodstoves) and fireplaces.



Woodstoves are commonly used in residences as space heaters. They are used both as the primary source of residential heat and to supplement conventional heating systems. Woodstoves have varying designs based on the use or non-use of baffles and catalysts, the extent of combustion chamber sealing, and differences in air intake and exhaust systems. Woodstove design and operation practices are important determinants of POM formation in wood-fired sources (Mead et al., 1986; Kelly, 1983).

The EPA has identified five categories of wood-burning devices based on differences in both the magnitude and the composition of the emissions (U.S. EPA, 1993b):

- Conventional woodstoves;
- Noncatalytic woodstoves;
- Catalytic woodstoves;
- Pellet stoves; and
- Masonry heaters.

Among these categories, there are many variations in device design and operation characteristics.

The conventional woodstove category comprises all stoves without catalytic combustors not included in the other noncatalytic categories (i.e., noncatalytic and pellet). Conventional woodstoves do not have any emissions reduction technology or design features and, in most cases, were manufactured before July 1, 1986. Stoves of many different airflow designs may be included in this category, such as updraft, downdraft, crossdraft and S-flow (U.S. EPA, 1993b).

Noncatalytic woodstoves are those units that do not employ catalysts but do have emissions-reducing technology or features. The typical noncatalytic design includes baffles and secondary combustion chambers (U.S. EPA, 1993b).

Catalytic woodstoves are equipped with a ceramic or metal honeycomb device, called a combustor or converter, that is coated with a noble metal such as platinum or palladium. The catalyst reduces the ignition temperature of the unburned VOC and CO in the exhaust gases, thus augmenting their ignition and combustion at normal stove operating temperatures. As these components of the gases burn, the temperature inside the catalyst increases to a point at which the ignition of the gases is essentially self-sustaining (U.S. EPA, 1993b).

Pellet stoves are fueled with pellets of sawdust, wood products, and other biomass materials pressed into manageable shapes and sizes. These stoves have active air flow systems and a unique grate design to accommodate this type of fuel. Some pellet stove models are subject to the 1988 New Source Performance Standards (NSPS); others are exempt because of their high air-to-fuel ratio (i.e., greater than 35-to-1) (U.S. EPA, 1993b).

The quantities and types of emissions from woodstoves are highly variable, depending on a number of factors such as stage of the combustion cycle and wood type. McCrillis and Watts concluded from emissions testing done on three woodstoves that increasing the burn rate (in terms of mass of wood burned per hour) resulted in increasing PAH emissions (in terms of mass of pollutant emitted per hour) (McCrillis and Watts, 1992a). Results from 14 tests conducted on conventional and catalytic woodstoves showed a similar trend of increasing PAH emissions with increasing burn rate (Burnet et al., 1990a).

Regarding wood type, McCrillis and Watts reported that PAH emissions were higher for stoves burning pine wood as compared to oak wood (McCrillis and Watts, 1992a). The same conclusion was drawn by Burnet et al., who statistically showed a main effect decrease in PAH emissions of 849 mg per hour, at a 99-percent confidence bound, in going from pine fuel to oak fuel (Burnet et al., 1990b).

Fireplaces are used primarily for aesthetic effects and secondarily as a supplemental heating source in houses and other dwellings. Wood is the most common fuel for fireplaces, but coal and densified wood “logs” may also be burned (U.S. EPA, 1993a). The user intermittently adds fuel to the fire by hand. Fireplaces are inefficient combustion devices, with

high uncontrolled excess air rates and no sort of secondary combustion. POM emissions result from the combination of free radical species formed in the flame zone, primarily as a consequence of incomplete combustion. Under reducing conditions, radical chain propagation is enhanced, allowing the buildup of complex organic material such as POM. The POM is generally found in or on smoke particles, although some sublimation into the vapor phase is probable.

Fireplace heating efficiency may be improved by a number of measures that either reduce the excess air rate or transfer back into the residence some of the heat that would normally be lost in the exhaust gases or through fireplace walls. As noted below, such measures are commonly incorporated into prefabricated units. As a result, the energy efficiencies of prefabricated fireplaces are slightly higher than those of masonry fireplaces (U.S. EPA, 1993a).

Prefabricated fireplaces are commonly equipped with louvers and glass doors to reduce the intake of combustion air, and some are surrounded by ducts through which floor-level air is drawn by natural convection, heated, and returned to the room. Many varieties of prefabricated fireplaces are now on the market. One general class is the free-standing fireplace, the most common of which consists of an inverted sheet metal funnel and stovepipe directly above the fire bed. Another class is the “zero clearance” fireplace, an iron or heavy-gauge steel firebox lined with firebrick and surrounded by multiple steel walls with spaces for air circulation. Some zero clearance fireplaces can be inserted into existing masonry fireplace openings, and thus are sometimes called “inserts.” Some of these units are equipped with close-fitting doors and have operating and combustion characteristics similar to those of woodstoves (U.S. EPA, 1993a).

#### Emission Factors--Residential Wood Combustion

POM is an important component of the condensable fraction of wood smoke. The POM in wood smoke contains a wide range of compounds, including organic compounds formed through incomplete combustion by the combination of free radical species in the flame zone. Emission factors for conventional, noncatalytic, catalytic, and exempt pellet woodstoves were compiled from various testing studies and reported by EPA (U.S. EPA, 1993b). The emission

factors are shown in Tables 4.1-1 through 4.1-4. No factors are reported for masonry heaters; however, it is probable that POM is emitted from these units as well.

There are fewer PAH emissions test data for fireplaces as compared to woodstoves. Factors for individual PAH species from the burning of oak and the burning of pine were obtained from the results of EPA's research program for controlling residential wood combustion emissions (Hall and DeAngelis, 1980). As part of that program, PAH emissions from fireplaces burning seasoned oak wood and green pine were measured. The emission factors developed from these measurements are shown in Table 4.1-5. Another set of emission factors collected as part of a literature review by Cooper (Cooper, 1980) is also shown in Table 4.1-5. The wood type used in the tests supporting those factors was not identified.

#### Process Description--Residential Coal Combustion

Coal is not a widely used source of fuel for residential heating purposes in the United States. Only 0.3 percent of the total coal consumption in 1990 was for residential use (Energy Information Administration, 1992). However, combustion units burning coal are sources of POM emissions and may be important local sources in areas that have a large number of residential houses that rely on this fuel for heating.

There are a wide variety of coal-burning stoves in use. These include boilers, furnaces, stoves that are designed to burn coal, and wood-burning stoves that burn coal. These units may be hand-fed or automatic feed. Boilers and warm-air furnaces are usually stoker-fed and are automatically controlled by a thermostat. The stove units are less sophisticated, generally hand-fed, and less energy efficient than boilers and furnaces. POM emissions from all these units depend strongly on combustion efficiency, which can vary widely from unit to unit. Higher POM emissions are typically associated with the stove-type units because they have lower combustion efficiencies (DeAngelis and Reznik, 1979).

TABLE 4.1-1. PAH EMISSION FACTORS FOR CONVENTIONAL WOODSTOVES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a</sup>	Emission Factor Rating
21-04-008-051	Conventional Woodstove	None	Benz(a)anthracene	0.020 (0.010)	E
			Benzo(a)pyrene	0.004 (0.002)	E
			Benzo(b)fluoranthene	0.006 (0.003)	E
			Benzo(k)fluoranthene	0.002 (0.001)	E
			Chrysene	0.012 (0.006)	E
			Dibenz(a,h)anthracene	0.000 (0.000)	E
			Indeno(1,2,3-cd)pyrene	0.000 (0.000)	E
			Acenaphthylene	0.212 (0.106)	E
			Acenaphthene	0.010 (0.005)	E
			Anthracene	0.014 (0.007)	E
			Benzo(ghi)perylene	0.004 (0.002)	E
Fluoranthene	0.020 (0.010)	E			

(continued)

TABLE 4.1-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a</sup>	Emission Factor Rating
21-04-008-051 (continued)	Conventional Woodstove (continued)	None	Fluorene	0.024 (0.012)	E
			Naphthalene	0.288 (0.144)	E
			Phenanthrene	0.078 (0.039)	E
			Pyrene	0.024 (0.012)	E
			Benzo(e)pyrene	0.012 (0.006)	E

<sup>a</sup>Factors are expressed as lb (g) of pollutant emitted per ton (kg) of wood combusted.

Source: U.S. EPA, 1993b.

TABLE 4.1-2. PAH EMISSION FACTORS FOR NONCATALYTIC WOODSTOVES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a</sup>	Emission Factor Rating
21-04-008-050	Noncatalytic Woodstove	Baffles and Secondary Combustion Chambers	Benz(a)anthracene	< 0.001 ( < 0.001)	E
			Benzo(a)pyrene	0.006 (0.003)	E
			Benzo(b)fluoranthene	0.004 (0.002)	E
			Benzo(k)fluoranthene	< 0.001 ( < 0.001)	E
			Chrysene	0.010 (0.005)	E
			Dibenz(a,h)anthracene	0.004 (0.002)	E
			Indeno(1,2,3-cd)pyrene	0.020 (0.010)	E
			Acenaphthylene	0.032 (0.016)	E
			Acenaphthene	0.010 (0.005)	E
			Anthracene	0.009 (0.004)	E
			Benzo(ghi)perylene	0.020 (0.010)	E
Fluoranthene	0.008 (0.004)	E			

(continued)

TABLE 4.1-2. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a</sup>	Emission Factor Rating
21-04-008-050 (continued)	Noncatalytic Woodstove (continued)	Baffles and Secondary Combustion Chambers (continued)	Fluorene	0.014 (0.007)	E
			Naphthalene	0.144 (0.072)	E
			Phenanthrene	0.118 (0.059)	E
			Pyrene	0.008 (0.004)	E
			Benzo(e)pyrene	0.002 (0.001)	E
			Benzo(ghi)fluoranthene	0.028 (0.014)	E
			Perylene	0.002 (0.001)	E
			Biphenyl	0.022 (0.011)	E
			7,12-Dimethylbenz(a)anthracene	0.004 (0.002)	E
			9-Methylanthracene	0.004 (0.002)	E
			12-Methylbenz(a)anthracene	0.002 (0.001)	E
3-Methylchloanthrene	< 0.001 (< 0.001)	E			

(continued)



TABLE 4.1-2. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a</sup>	Emission Factor Rating
21-04-008-050 (continued)	Noncatalytic Woodstove (continued)	Baffles and Secondary Combustion Chambers (continued)	1-Methylphenanthrene	0.030 (0.015)	E
			Nitronaphthalene	0.000 (0.000)	E
			Phenanthrol	0.000 (0.000)	E

<sup>a</sup>Factors are expressed as lb (g) of pollutant emitted per ton (kg) of wood combusted.

Source: U.S. EPA, 1993b.

TABLE 4.1-3. PAH EMISSION FACTORS FOR CATALYTIC WOODSTOVES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a</sup>	Emission Factor Rating
21-04-008-030	Catalytic Woodstove	Catalytic Converter	Benz(a)anthracene	0.024 (0.012)	E
			Benzo(a)pyrene	0.004 (0.002)	E
			Benzo(b)fluoranthene	0.004 (0.002)	E
			Benzo(k)fluoranthene	0.002 (0.001)	E
			Chrysene	0.010 (0.005)	E
			Dibenz(a,h)anthracene	0.002 (0.001)	E
			Indeno(1,2,3-cd)pyrene	0.004 (0.002)	E
			Acenaphthylene	0.068 (0.034)	E
			Acenaphthene	0.006 (0.003)	E
			Anthracene	0.008 (0.004)	E
			Benzo(ghi)perylene	0.002 (0.001)	E
			Fluoranthene	0.012 (0.006)	E

(continued)

TABLE 4.1-3. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a</sup>	Emission Factor Rating
21-04-008-030 (continued)	Catalytic Woodstove (continued)	Catalytic Converter (continued)	Fluorene	0.014 (0.007)	E
			Naphthalene	0.186 (0.093)	E
			Phenanthrene	0.489 (0.024)	E
			Pyrene	0.010 (0.005)	E
			Benzo(e)pyrene	0.004 (0.002)	E
			Benzo(ghi)fluoranthene	0.006 (0.003)	E

<sup>a</sup>Factors are expressed as lb (g) of pollutant emitted per ton (kg) of wood combusted.

Source: U.S. EPA, 1993b.

TABLE 4.1-4. PAH EMISSION FACTORS FOR PELLET STOVES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a,b</sup>	Emission Factor Rating
21-04-008-030	Pellet Stove	None	Benzo(b)fluoranthene	2.60E-05 (1.30E-05)	E
			Chrysene	7.52E-05 (3.76E-05)	E
			Fluoranthene	5.48E-05 (2.74E-05)	E
			Phenanthrene	3.32E-05 (1.66E-05)	E
			Pyrene	4.84E-05 (2.42E-05)	E

<sup>a</sup>Emission factors are for pellet stoves that are exempt from the 1988 NSPS.

<sup>b</sup>Factors are expressed as lb (g) of pollutant emitted per ton (kg) of pellets combusted.

Source: U.S. EPA, 1993b.

TABLE 4.1-5. PAH EMISSION FACTORS FOR FIREPLACES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/kg) <sup>a</sup>	Emission Factor Rating	Reference
21-04-008-001	Fireplace Burning Seasoned Oak	None	Benz(a)anthracene/Chrysene	4.00E-03 (2.00)	E	Hall et al., 1980
			Benzofluoranthenes	4.40E-03 (2.20)	E	Hall et al., 1980
			Anthracene/Phenanthrene	2.28E-02 (11.40)	E	Hall et al., 1980
			Fluoranthene	5.20E-03 (2.60)	E	Hall et al., 1980
			Benzo(ghi)perylene	2.60E-03 (1.30)	E	Hall et al., 1980
			Pyrene	5.20E-03 (2.60)	E	Hall et al., 1980
			Methyl anthracenes, phenanthrenes	6.80E-03 (3.40)	E	Hall et al., 1980
			Methyl fluoranthenes, pyrenes	4.60E-03 (2.30)	E	Hall et al., 1980
			Benzo(ghi)fluoranthene	1.80E-03 (0.90)	E	Hall et al., 1980
			Benzopyrenes/Perylene	3.40E-03 (1.70)	E	Hall et al., 1980
			Cyclopenta(cd)pyrene	2.00E-03 (1.00)	E	Hall et al., 1980

(continued)

TABLE 4.1-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/kg) <sup>a</sup>	Emission Factor Rating	Reference
21-04-008-001 (continued)	Fireplace Burning Seasoned Oak (continued)	None	Benzo(c)phenanthrene	8.00E-04 (0.40)	E	Hall et al., 1980
			C2-alkyl-anthracenes, -phenanthrenes	2.20E-03 (1.10)	E	Hall et al., 1980
			Cyclopenta-anthracenes, -phenanthrenes	8.00E-04 (0.40)	E	Hall et al., 1980
			Methyl-benzanthracenes, -benzphenanthrenes, -chrysenes	2.60E-03 (1.30)	E	Hall et al., 1980
			C2-alkyl-benzanthracenes- benzophenanthrenes-chrysenes	1.80E-02 (9.00)	E	Hall et al., 1980
			Dibenzanthracenes, -phenanthrenes	6.00E-04 (0.30)	E	Hall et al., 1980
			Dibenzopyrenes	1.40E-03 (0.70)	E	Hall et al., 1980
21-04-008-001 (continued)	Fireplace Burning Green Pine	None	Benz(a)anthracene/Chrysene	2.80E-03 (1.40)	E	Hall et al., 1980
			Benzofluoranthenes	3.20E-03 (1.60)	E	Hall et al., 1980
			Anthracene/Phenanthrene	1.38E-02 (6.90)	E	Hall et al., 1980
			Fluoranthene	3.20E-03 (1.60)	E	Hall et al., 1980

(continued)

TABLE 4.1-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/kg) <sup>a</sup>	Emission Factor Rating	Reference
21-04-008-001 (continued)	Fireplace - Burning Green Pine (continued)	None	Benzo(ghi)perylene	3.00E-03 (1.50)	E	Hall et al., 1980
			Pyrene	3.20E-03 (1.60)	E	Hall et al., 1980
			Methyl anthracenes, phenanthrenes	1.66E-02 (8.30)	E	Hall et al., 1980
			Methyl fluoranthenes, pyrenes	3.20E-03 (1.60)	E	Hall et al., 1980
			Benzo(ghi)fluoranthene	2.80E-03 (1.40)	E	Hall et al., 1980
			Benzopyrenes/Perylene	2.80E-03 (1.40)	E	Hall et al., 1980
			Cyclopenta(cd)pyrene	2.80E-03 (1.40)	E	Hall et al., 1980
			Benzo(c)phenanthrene	2.60E-03 (1.30)	E	Hall et al., 1980
			C2-alkyl-anthracenes, -phenanthrenes	2.80E-03 (1.40)	E	Hall et al., 1980
			Cyclopenta-anthracenes, -phenanthrenes	2.80E-03 (1.40)	E	Hall et al., 1980
			Methyl-benzanthracenes, -benzphenanthrenes, -chrysenes	3.20E-03 (1.60)	E	Hall et al., 1980
C2-alkyl-benzanthracenes- benzophenanthrenes-chrysenes	2.80E-03 (1.40)	E	Hall et al., 1980			

(continued)

TABLE 4.1-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/kg) <sup>a</sup>	Emission Factor Rating	Reference
21-04-008-001 (continued)	Fireplace - Burning Green Pine (continued)	None	Dibenzanthracenes, -phenanthrenes	1.00E-04 (0.05)	E	Hall et al. , 1980
			Dibenzopyrenes	2.00E-04 (0.10)	E	Hall et al. , 1980
21-04-008-001	Fireplace - Wood Type Unspecified	None	Benz(a)anthracene	3.80E-03 (1.90)	U	Cooper, 1980
			Benzo(a)pyrene	1.46E-03 (0.73)	U	Cooper, 1980
			Benzo(a)fluoranthenes	3.80E-03 (1.90)	U	Cooper, 1980
			Acenaphthene	2.40E-03 (1.20)	U	Cooper, 1980
			Acenaphthylene	2.00E-02 (10.00)	U	Cooper, 1980
			Anthracene/Phenanthrene	1.76E-02 (8.80)	U	Cooper, 1980
			Benzo(ghi)perylene	2.80E-03 (1.40)	U	Cooper, 1980
			Fluoranthene	3.20E-03 (1.60)	U	Cooper, 1980
			Fluorene	9.40E-03 (4.70)	U	Cooper, 1980

(continued)



TABLE 4.1-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/kg) <sup>a</sup>	Emission Factor Rating	Reference
21-04-008-001 (continued)	Fireplace - Wood Type Unspecified (continued)	None	Pyrene	3.20E-03 (1.60)	U	Cooper, 1980
			Dibenzanthracenes	3.60E-04 (0.18)	U	Cooper, 1980

<sup>a</sup>Factors are expressed as lb (mg) of pollutant emitted per ton (kg) of wood combusted.

POM emissions for residential coal combustion also depend on the type of coal being burned. DeAngelis et al., found that POM emissions increased as volatile content increased. Other studies report that anthracite coal generated lower POM emissions than bituminous coal (Giammer et al., 1976; and Sanborn et al., 1985).

#### Emission Factors--Residential Coal Combustion

DeAngelis and Reznik, reported average POM emission rates for a coal-burning boiler and furnace. These emission rates, shown in Table 4.1-6, represent the total of both particulate- and gas-phase POM. Both the boiler and the furnace were burning bituminous coal. POM emissions were much higher during the “off” position of the furnace than during the “on” position because air flow was reduced during the “off” position. They also showed that excess air flow reduced POM emissions (DeAngelis and Reznik, 1979).

PAH emission factors for residential coal combustion in stoves were reported in an emissions inventory study of Canada and the northeastern United States (Johnson et al., 1990b). The emission factors reported in that study were developed from emissions testing of three woodstoves (Sanborn, 1985). These factors are shown in Table 4.1-7. The testing was conducted on a coal stove and a woodstove burning both bituminous and anthracite coal. The factors represent the total of particulate- and gas-phase POM.

#### Process Description--Residential Distillate Oil Combustion

Distillate oil is the second most important home heating fuel behind natural gas (McCrillis and Watts, 1992b). The use of distillate oil-fired heating units is concentrated in the northeastern portion of the United States. In 1991, Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont, Delaware, District of Columbia, Maryland, New Jersey, New York, and Pennsylvania accounted for approximately 72 percent of the residential share of distillate oil sales (Energy Information Administration, 1991).

TABLE 4.1-6. PAH EMISSION FACTORS FOR RESIDENTIAL COAL BOILERS AND FURNACES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a</sup>	Emission Factor Rating
21-04-002-000	Bituminous/Subbituminous Coal Boilers and Furnaces	None	Benzopyrenes and Perylene	6.01E-03 (3.00E-03)	E
			Benzofluoranthene(s)	8.02E-03 (4.00E-03)	E
			Chrysene/Benz(a)anthracene	8.02E-03 (4.00E-03)	E
			Dibenz(a,h)anthracene	6.01E-03 (3.00E-03)	E
			Indeno(1,2,3-cd)pyrene	4.01E-03 (2.00E-03)	E
			Anthracene/Phenanthrene	3.21E-02 (1.60E-02)	E
			Fluoranthene	1.00E-02 (5.00E-03)	E
			Pyrene	1.00E-02 (5.00E-03)	E
			Benzo(c)phenanthrene	4.01E-04 (2.00E-04)	E
			7,12-Dimethylbenz(a)anthracene	1.66E-01 (8.30E-02)	E
9-Methylanthracene	4.01E-04 (2.00E-04)	E			
Dimethylanthracenes, phenanthrenes	1.60E-02 (8.00E-03)	E			

(continued)

TABLE 4.1-6. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (g/kg) <sup>a</sup>	Emission Factor Rating
21-04-002-000 (continued)	Bituminous/Subbituminous Coal Boilers and Furnaces (continued)	None	Methylanthracenes, phenanthrenes	2.00E-02 (1.00E-02)	E
			3-Methylchloanthrene	4.01E-03 (2.00E-03)	E
			Dibenzothiophene	4.01E-04 (2.00E-04)	E
			Methylfluoranthenes, pyrenes	6.01E-03 (3.00E-03)	E
			Dibenzo(c,g) carbazole	0.00 (< 0.0001)	E
			Dibenzopyrenes	1.80E-02 (9.00E-03)	E
			Methylchrysenes	1.00E-03 (5.00E-03)	E
			C <sub>4</sub> -Alkylphenanthrene	4.01E-03 (2.00E-03)	E

<sup>a</sup>Factors are expressed as lb (g) of pollutant emitted per ton (kg) of wood combusted.

Source: DeAngelis and Reznik, 1979.

TABLE 4.1-7. PAH EMISSION FACTORS FOR RESIDENTIAL COAL STOVES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating
21-04-002-000	Bituminous/Subbituminous Coal Stove	None	Benz(a)anthracene	6.01E-03 (3,000.00)	E
			Benzo(a)pyrene	5.21E-03 (2,600.00)	E
			Chrysene	5.61E-03 (2,800.00)	E
			Acenaphthylene	2.40E-02 (12,000.00)	E
			Anthracene	6.21E-03 (3,100.00)	E
			Phenanthrene	2.20E-02 (11,000.00)	E
			Benzo(e)pyrene	4.01E-03 (2,000.00)	E
21-04-001-000	Anthracite Coal	None	Benz(a)anthracene	7.01E-05 (35.00)	E
			Benzo(a)pyrene	6.41E-06 (3.20)	E
			Chrysene	6.41E-05 (32.00)	E
			Acenaphthene	2.61E-05 (13.00)	E
			Acenaphthylene	1.18E-04 (59.00)	E

(continued)

TABLE 4.1-7. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating
21-04-001-000 (continued)	Anthracite Coal (continued)	None	Anthracene	2.81E-05 (14.00)	E
			Fluorene	3.01E-05 (15.00)	E
			Phenanthrene	2.75E-04 (137.00)	E
			Benzo(e)pyrene	7.62E-06 (3.80)	E

<sup>a</sup>Factors are expressed as lb (mg) of pollutant emitted per ton (Mg) of coal combusted.

Source: Johnson et al., 1990b.

Residential oil-fired heating units are available in a number of design and operating variations. These variations are related to burner and combustion chamber design, excess air, heating medium, etc. Residential systems typically operate only in an “on” or “off” mode and at a constant fuel-firing rate, as opposed to commercial and industrial applications, where load modulation is used (Suprenant et al., 1979). In distillate oil-fired heating units, pressure or vaporization is used to atomize fuel oil in an effort to produce finer droplets for combustion. Finer droplets generally mean more complete combustion and less POM formation.

When properly tuned, residential oil furnaces are relatively clean-burning, especially as compared to woodstoves (McCrillis and Watts, 1992b). However, Steiber and McCrillis (1991) have shown that, in practice, not all of the fuel oil is burned and tiny droplets escape the flame and are carried out in the exhaust. Steiber and McCrillis also concluded that most of the organic emissions from an oil furnace are due to the unburned oil as opposed to soot from the combustion process; especially in the more modern burners that use a retention head burner, where over 90 percent of the carbon in the emissions was from unburned fuel (Steiber and McCrillis, 1991).

#### Emission Factors--Residential Distillate Oil Combustion

Emission factors for PAH from distillate oil-fired heating units were compiled as part of a Canadian inventory study (Johnson et al., 1990b). The factors reported in that study were derived from two sources: testing of two pressure-atomized and one vaporized unit by Hagenbrauk (1967) and the results of a literature search (Smith, 1984) which identified emission factors for one pressure-atomized and one vaporized unit. The factors reported in the Johnson et al. inventory are shown in Table 4.1-8.

#### Process Description--Residential Natural Gas Combustion

Natural gas is the fuel most widely used for home heating purposes, with more than half of all homes being heated through natural gas combustion (Ryan and McCrillis, 1994). Gas-fired residential heating systems are generally less complex and easier to maintain than

TABLE 4.1-8. PAH EMISSION FACTORS FOR RESIDENTIAL OIL-FIRED COMBUSTION SOURCES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1000 gal (mg/kL) <sup>a</sup>	Emission Factor Rating
21-04-004-000	Distillate (No. 2 Oil) Oil-Fired Furnaces (average of atomized and vaporized units)	None	Benz(a)anthracene	5.44E-04 (65.00)	E
			Benzo(a)pyrene	1.92E-05 (2.30)	E
			Anthracene	ND	E
			Benzo(ghi)perylene	5.02E-05 (6.00)	E
			Fluoranthene	3.93E-03 (470.00)	E
			Phenanthrene	1.00E-03 (120.00)	E
			Pyrene	1.42E-03 (170.00)	E
			Benzo(e)pyrene	1.25E-04 (15.00)	E
			Coronene	3.60E-05 (4.30)	E
			Perylene	7.53E-06 (0.90)	E

<sup>a</sup>Factors are expressed as lb (mg) of pollutant emitted per 1,000 gal (kL) of oil combusted.

ND = not detected.

Source: Johnson et al., 1990b.



oil-burning units because the fuel burns more cleanly and no atomization is required. Most residential gas burners are typically of the same basic design. Natural aspiration is used where the primary air mixes with the gas as it passes through the distribution pipes. Secondary air enters the furnace around the burners. Flue gases then pass through a heat exchanger and a stack. As with oil-fired systems, there is usually no pollution control equipment installed on gas systems, and excess air, residence time, flame retention devices, and maintenance are the key factors in the control of emissions from these units.

#### Emission Factors--Residential Natural Gas Combustion

Emissions testing for PAH from gas-fired residential units has been extremely scarce, probably because the expected emissions are low and this source has not been identified as a priority for testing. Based on emission factors relative to thermal input, Ryan and McCrillis concluded that residential natural gas emissions are at least a factor of 10 to 100 less than comparable emissions from residential oil furnaces and woodstoves (Ryan and McCrillis, 1994). As part of the study quantifiable amounts of specific PAH compounds were measured from two natural gas, forced-air furnaces and emission factors were developed.

One of the furnaces was a 15 to 20 year old, horizontal forced-air furnace with a medium efficiency rating of between 60 to 70 percent. The second furnace tested was a new, modern, high-efficiency furnace with an energy efficiency rating of 94 percent. The units were configured and operated to match a residential-type setting. Based on their results, the study team concluded that detection limits for many of the PAH compounds were inadequate to accurately estimate emission factors for a large majority of the PAH compounds. The team did, however, report emission factors for a limited number of PAHs that were measured above the detection limit. These factors are presented in Table 4.1-9.

#### Process Description--Residential Kerosene Combustion

The sale and use of kerosene space heaters increased dramatically during the 1980s (Traynor et al., 1990). They continue to be sold and used throughout the United States as

TABLE 4.1-9. PAH EMISSION FACTORS FOR RESIDENTIAL NATURAL GAS-FIRED COMBUSTION SOURCES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/10 <sup>12</sup> Btu (pg/kJ) <sup>a</sup>	Emission Factor Rating
21-04-006-000	Natural Gas-Fired, Horizontal Forced-Air Furnace, Rated at 120,000 Btu/hr	None	Benz(a)anthracene	9.33E-02 (40.00)	E
			Chrysene	3.96E-02 (17.00)	E
			Fluoranthene	4.90E-02 (21.00)	E
			Pyrene	6.99E-02 (30.00)	E
21-04-006-000	Modern, High-Efficiency, Natural Gas-Fired, Vertical, Condensing Up-Flow Forced-Air Furnace Rated at 50,000 Btu/hr	None	Benz(a)anthracene	1.10E-01 (47.00)	E
			Benzo(a)pyrene	8.39E-02 (36.00)	E
			Benzo(b)fluoranthene	1.21E-01 (52.00)	E
			Benzo(k)fluoranthene	1.21E-01 (52.00)	E
			Chrysene	1.21E-01 (52.00)	E
			Indeno(1,2,3-cd)pyrene	6.53E-02 (28.00)	E
			Dibenz(a,h)anthracene	4.43E-02 (19.00)	E

(continued)

TABLE 4.1-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/10 <sup>12</sup> Btu (pg/kJ) <sup>a</sup>	Emission Factor Rating
21-04-006-000 (continued)	Modern, High-Efficiency, Natural Gas-Fired, Vertical, Condensing Up-Flow Forced-Air Furnace Rated at 50,000 Btu/hr (continued)	None	Benzo(ghi)perylene	1.35E-01 (58.00)	E
			Fluoranthene	5.13E-02 (22.00)	E
			Phenanthrene	9.79E-02 (42.00)	E
			Pyrene	6.53E-02 (28.00)	E

<sup>a</sup>Factors are expressed in lb (pg) of pollutant emitted per 10<sup>12</sup> Btu (kJ) of natural gas combusted.

Source: Ryan et al., 1994.

supplementary home heating sources and, in some cases, as primary heating sources. These units are usually unvented and release emissions inside the home, with some emissions eventually escaping to the atmosphere. There are two basic types of kerosene space heaters: convective and radiant.

#### Emission Factors--Residential Kerosene Combustion

Traynor et al. investigated emissions from both types of kerosene space heaters (Traynor et al., 1990). Particulate PAH emission rates were developed for a radiant heater operating under well-tuned conditions and a convective heater operating under poorly tuned conditions. These emission rates are shown in Table 4.1-10. The study team concluded that kerosene heaters can emit PAHs and nitrated PAHs. Naphthalene was the primary PAH emitted from both types of heaters. Relatively few PAHs were observed in this study, but that may be due to the use of a very broad GC/MS scanning technique; other PAHs would probably have been found by a more sensitive technique.

TABLE 4.1-10. PAH EMISSION FACTORS FOR RESIDENTIAL KEROSENE HEATERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/10E+12 Btu (ng/kJ) <sup>a</sup>	Emission Factor Rating
21-04-011-000	Radiant Kerosene Space Heater - Well-tuned	None	Chrysene	0.02 (0.01)	E
			Fluoranthene	0.05 (0.02)	E
			Naphthalene	18.65 (8.00)	E
			Phenanthrene	0.70 (0.30)	E
21-04-011-000	Convective Kerosene Space Heater - Maltuned	None	Anthracene	0.70 (0.30)	E
			Fluoranthene	0.70 (0.30)	E
			Naphthalene	53.62 (23.00)	E
			Phenanthrene	2.10 (0.90)	E

<sup>a</sup>Factors are expressed in lb (ng) of pollutant emitted per 10E+12 Btu (kJ) of kerosene combusted.

Source: Traynor et al., 1990.

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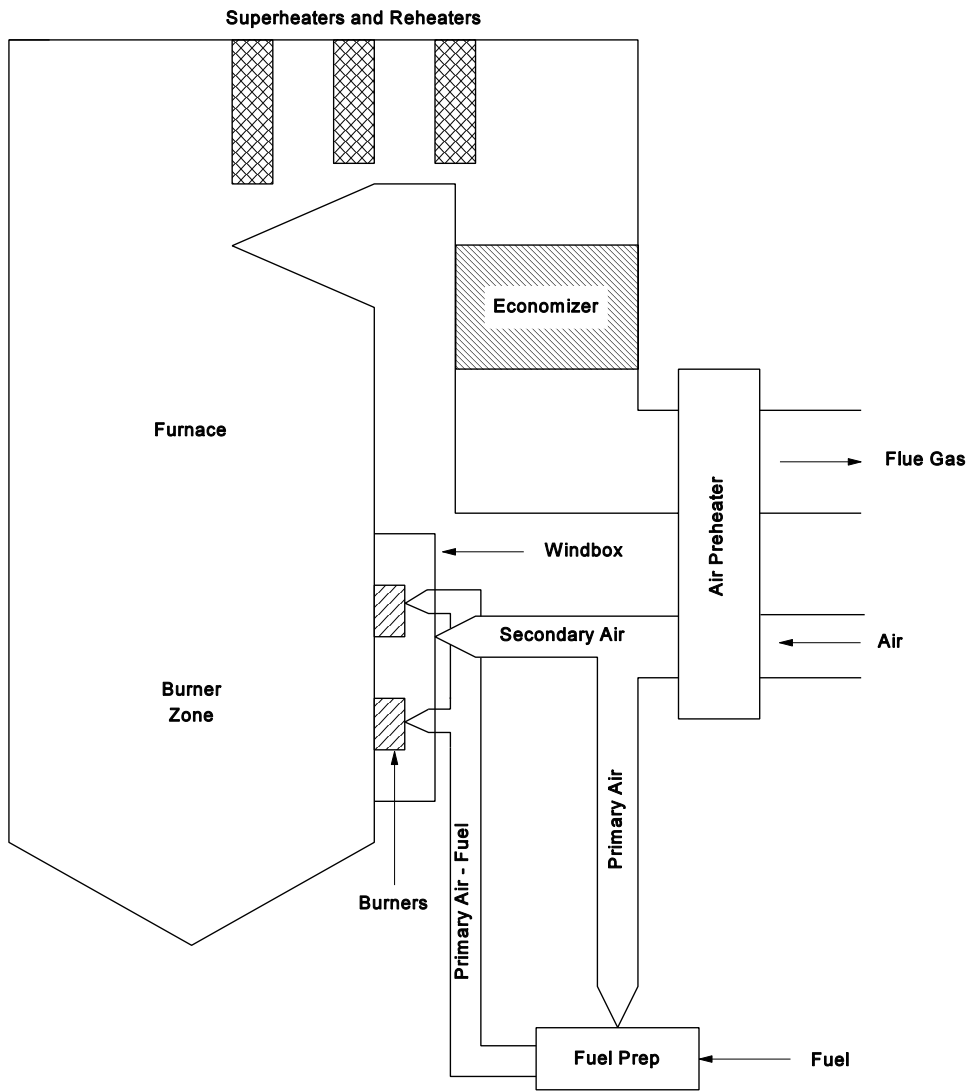
#### 4.1.2 Utility, Industrial and Commercial Fuel Combustion

##### Process Description--Utility Sector

Utility boilers burn coal, oil, and natural gas to generate steam for electricity generation. Fossil fuel-fired utility boilers comprise about 72 percent (or 497,000 megawatts [MW]) of the generating capacity of U.S. electric power plants. Of these fuels, coal is the most widely used, accounting for 60 percent of the U.S. fossil fuel generating capacity. Natural gas represents about 25 percent and oil represents 15 percent of the U.S. fossil fuel generating capacity (U.S. EPA, 1994a).

A utility boiler consists of several major subassemblies, as shown in Figure 4.1.2-1. These subassemblies include the fuel preparation system, air supply system, burners, the furnace, and the convective heat transfer system. The fuel preparation system, air supply, and burners are primarily involved in converting fuel into thermal energy in the form of hot combustion gases. The furnace and convective heat transfer system are involved in the transfer of the thermal energy in the combustion gases to the superheated steam required to operate the steam turbine and produce electricity (U.S. EPA, 1994a).

Three key thermal processes occur in the furnace and convective sections of the boiler. First, thermal energy is released during controlled mixing and combustion of fuel and oxygen in the burners and furnace. Second, a portion of the thermal energy formed by combustion is adsorbed as radiant energy by the furnace walls. The furnace walls are formed by multiple, closely-spaced tubes, which carry high-pressure water from the bottom of the furnace to absorb radiant heat energy to the steam drum located at the top of the boiler. Third, the gases enter the convective pass of the boiler, and the balance of the energy retained by the high-temperature gases is adsorbed as convective energy by the convective heat transfer system (superheater, reheater, economizer, and air preheater) (U.S. EPA, 1994a).



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Figure 4.1.2-1. Simplified Boiler Schematic

Source: U.S. EPA, 199a.

Utility boilers are generally identified by their furnace configuration. Different furnace configurations used in utility boilers include tangentially-fired, wall-fired, cyclone-fired, stoker-fired, and fluidized bed combustion (FBC) boilers. Some of these furnace configurations are designed primarily for coal combustion, while others are designed for coal, oil, or natural gas combustion. The types of furnaces most commonly used for firing oil and natural gas are the tangentially-fired and wall-fired boiler designs (Shih et al., 1980). One of the primary differences between furnaces designed to burn coal versus oil or gas is the furnace size. Coal requires the largest furnace, followed by oil, then gas (U.S. EPA, 1994a).

The average size of boilers used in the utility sector varies primarily according to boiler type. Cyclone-fired boilers are generally the largest, averaging about 250 to 380 MW generating capacity. Tangentially-fired and wall-fired boiler designs firing coal average about 120 to 430 MW, while these designs firing oil and natural gas average about 100 to 270 MW. Stoker-fired boilers average about 10 to 17 MW (Shih et al., 1980). Additionally, unit sizes of FBC boilers range from 25 to 400 MW, with the largest FBC boilers typically closer to 200 MW (U.S. EPA, 1994a).

Tangentially-fired Boiler--The tangentially-fired boiler is based on the concept of a single flame zone within the furnace. The fuel-air mixture in a tangentially-fired boiler projects from the four corners of the furnace along a line tangential to an imaginary cylinder located along the furnace centerline. When coal is used as the fuel, the coal is pulverized in a mill to the consistency of talcum powder (i.e., at least 70 percent of the particles will pass through a 200 mesh sieve), entrained in primary air, and fired in suspension (U.S. EPA, 1995a). As fuel and air are fed to the burners, a rotating "fireball" is formed, which may be moved up and down by tilting the fuel-air nozzle assembly, to control the furnace exit gas temperature and provide steam temperature control during variations in load. Tangentially-fired boilers commonly burn coal (pulverized). However, oil or gas may also be burned (U.S. EPA, 1994a).

Wall-fired Boiler--Wall-fired boilers are characterized by multiple individual burners located on a single wall or on opposing walls of the furnace (Figure 4.1.2-2). As with tangential-fired

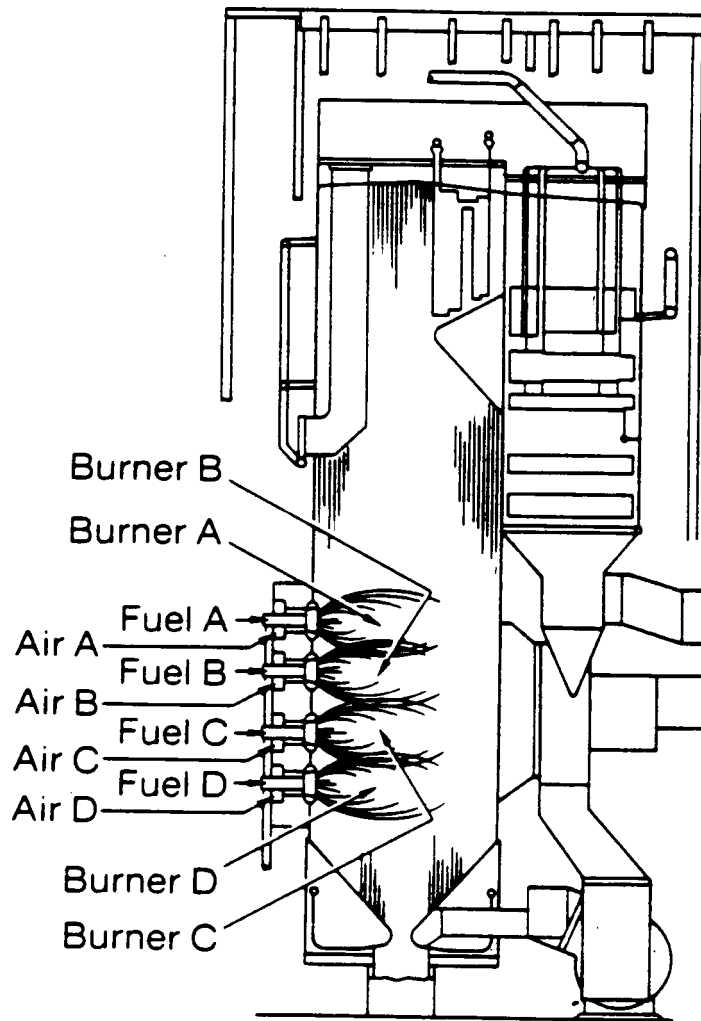


Figure 4.1.2-2. Single Wall-Fired Boiler

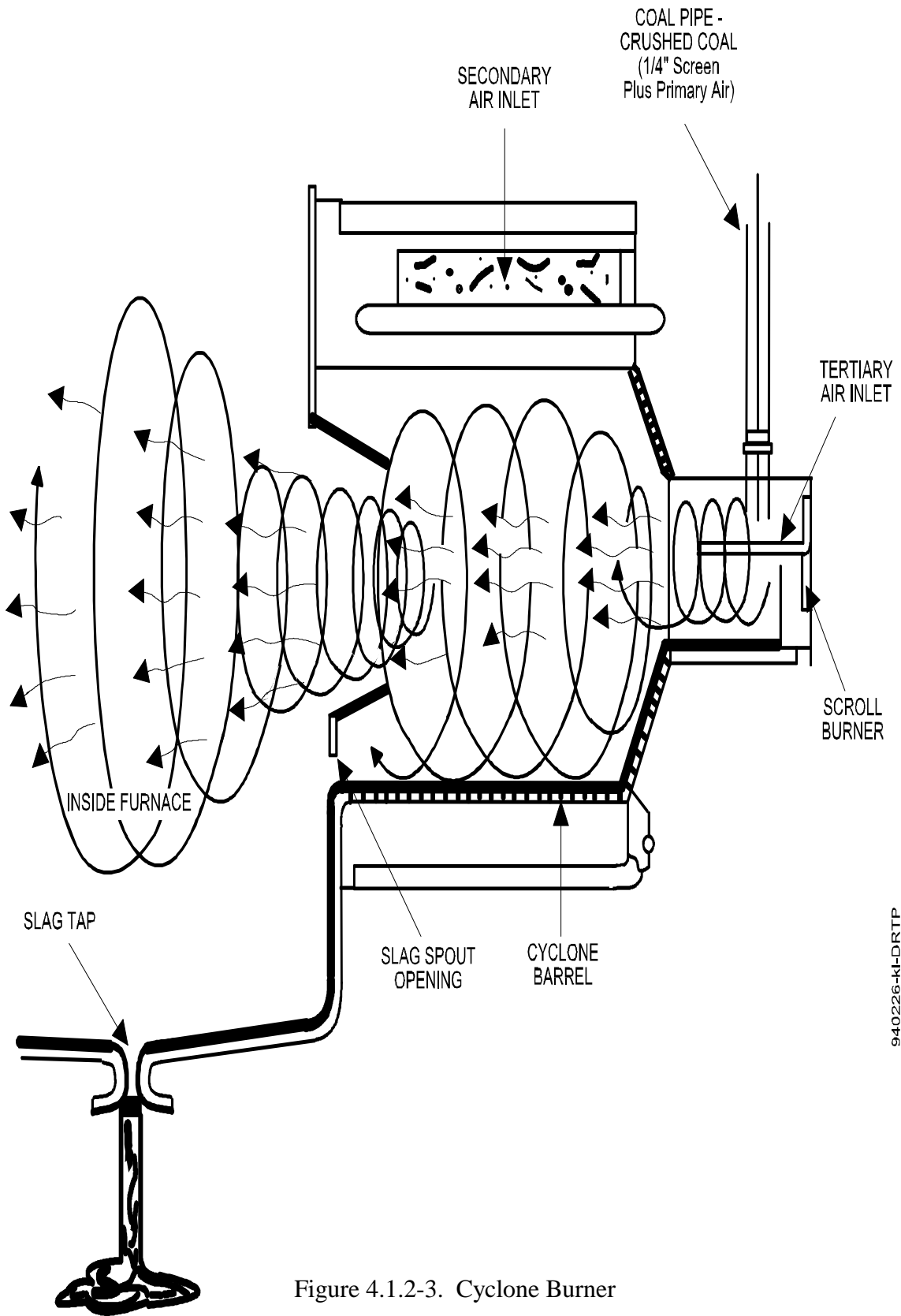
Source: U.S. EPA, 1994a.

boilers, when coal is used as the fuel, the coal is pulverized, entrained in primary air, and fired in suspension. In contrast to tangentially-fired boilers that produce a single flame envelope, or fireball, each of the burners in a wall-fired boiler has a relatively distinct flame zone. Depending on the design and location of the burners, wall-fired boilers consist of various designs, including single-wall, opposed-wall, cell, vertical, arch, and turbo. Wall-fired boilers may burn coal (pulverized), oil, or natural gas (U.S. EPA, 1994a).

Cyclone-fired Boiler--In cyclone-fired boilers, fuel and air are burned in horizontal, cylindrical chambers, producing a spinning, high-temperature flame (Figure 4.1.2-3). When coal is used, the coal is crushed (rather than pulverized) to a 4-mesh size and admitted with the primary air in a tangential fashion. The finer coal particles are burned in suspension, while the coarser particles are thrown to the walls by centrifugal force (Shih et al., 1980). Cyclone-fired boilers are almost exclusively coal-fired. However, some units are also able to fire oil and natural gas (U.S. EPA, 1994a).

Fluidized Bed Combustion Boiler--Fluidized bed combustion (FBC) is a newer boiler technology that is not as widely used as the other, conventional boiler types. In a typical FBC boiler, crushed coal in combination with inert material (sand, silica, alumina, or ash) and/or sorbent (limestone) is maintained in a highly turbulent suspended state by the upward flow of primary air from the windbox located directly below the combustion floor (Figure 4.1.2-4). This fluidized state provides a large amount of surface contact between the air and solid particles, which promotes uniform and efficient combustion at lower furnace temperatures, 1,575 to 1,650°F (860 to 900°C) compared to 2,500 to 2,800°F (1,370 to 1,540°C) for conventional coal-fired boilers. Fluidized bed combustion boilers have been developed to operate at both atmospheric and pressurized conditions (U.S. EPA, 1994a).

Stoker-fired Boiler--Instead of firing coal in suspension, as practiced by the boilers described above, mechanical stokers can be used to burn coal in fuel beds. All mechanical stokers are designed to feed coal onto a grate within the furnace. The most common stoker type of boiler used in the utility industry is the spreader stoker (Figure 4.1.2-5). Other stoker types are



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Figure 4.1.2-3. Cyclone Burner

Source: U.S. EPA, 1994a.

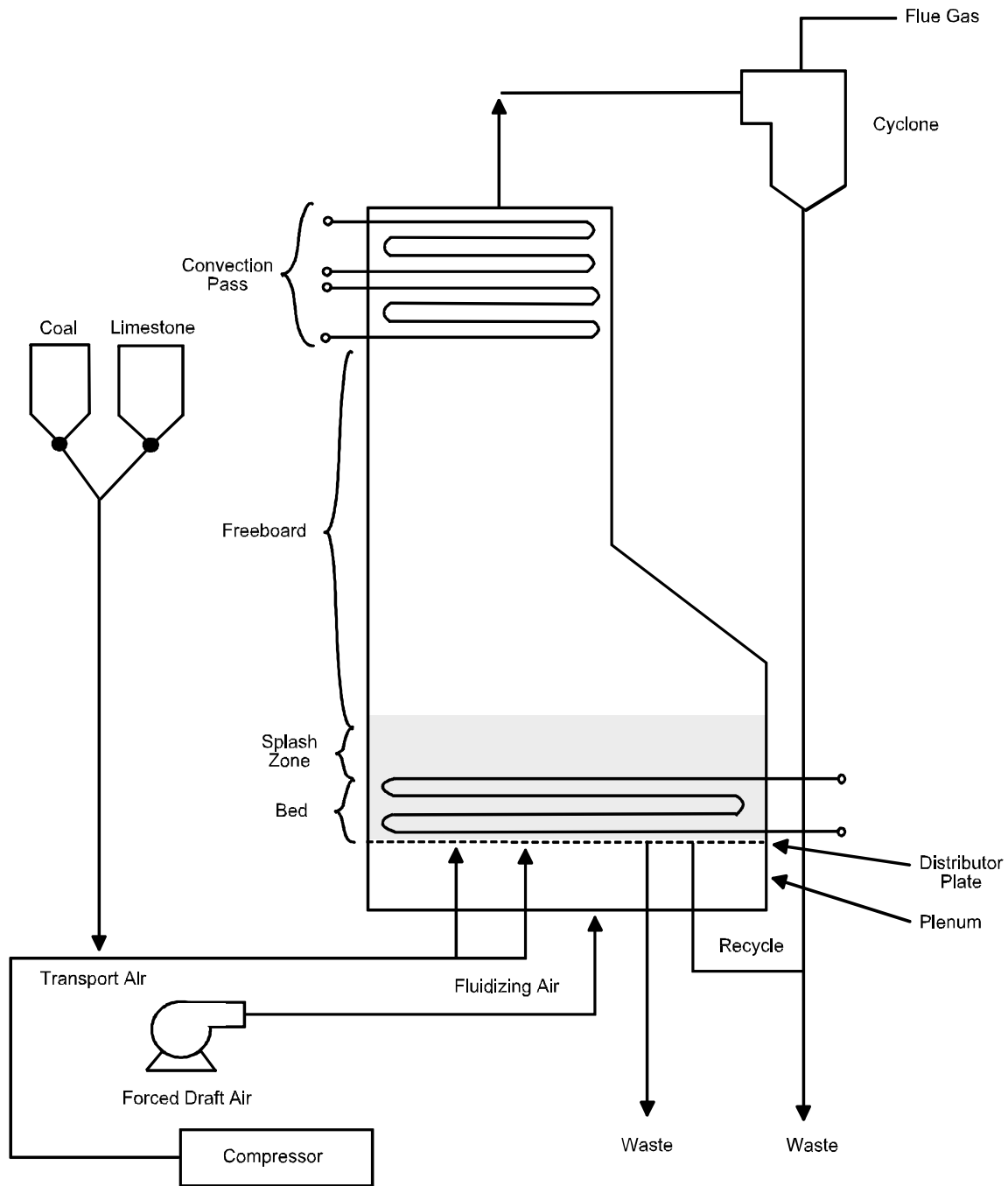


Figure 4.1.2-4. Simplified Atmospheric Fluidized Bed Combustor Process Flow Diagram

Source: U.S. EPA, 1994a.

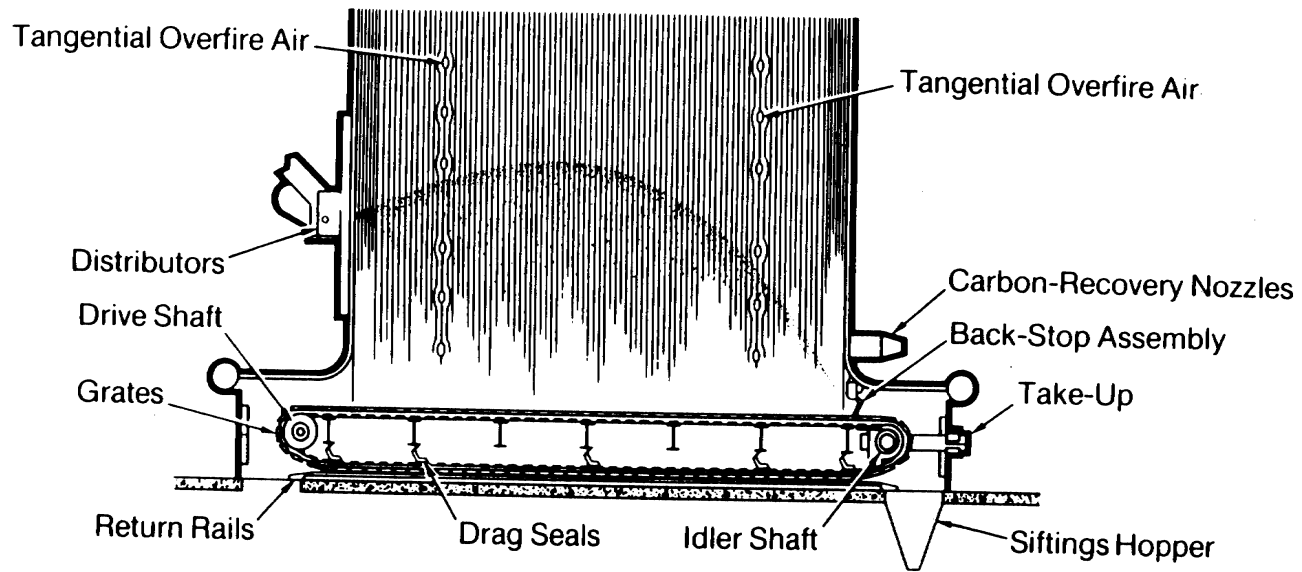


Figure 4.1.2-5. Spreader Type Stoker-fired Boiler

Source: U.S. EPA, 1994a.



overfeed and underfeed stokers. In spreader stokers, a flipping mechanism throws crushed coal into the overfeed and underfeed stokers. In spreader stokers, a flipping mechanism throws crushed coal into the furnace and onto a moving fuel bed (grate). Combustion occurs partly in suspension and partly on the grate (U.S. EPA, 1995a). In overfeed stokers, crushed coal is fed onto a traveling or vibrating grate from an adjustable gate above and burns on the fuel bed as it progresses through the furnace. Conversely, in underfeed stokers, crushed coal is forced upward onto the fuel bed from below by mechanical rams or screw conveyors (U.S. EPA, 1995a; U.S. EPA, 1994a).

Emission Control Techniques--Utility boilers are highly efficient and generally the best controlled of all combustion sources. Existing emission regulations for total particulate matter (PM), nitrogen oxides ( $\text{NO}_x$ ), and sulfur dioxide ( $\text{SO}_2$ ) have necessitated controls on coal-, oil-, and gas-fired utility sources. Oil-fired units are not controlled for  $\text{SO}_2$  other than by choice of fuel sulfur content (i.e., no add-on controls for oil). Emission controls for PM and  $\text{SO}_2$  are not required on natural gas boilers because uncontrolled emissions are inherently low relative to coal and oil units (Kelly, 1983). Baghouses, ESPs, wet scrubbers, and multicyclones have been applied for PM control in the utility sector. Particulate POM, particularly fine particles, would be controlled most effectively by baghouses or ESPs. No control of gaseous POMs would be achieved by baghouse and ESP systems. Wet scrubbers could potentially be effective for controlling particulate and gaseous POM. Scrubbers would condense the POM compounds existing as vapors and collect them as the gas stream is saturated in the scrubber. Multicyclones would be the poorest control system for POM emissions because they are ineffective on fine particles and would offer no reduction of gaseous POM (Mead et al., 1986; Kelly, 1983).

Nitrogen oxide control techniques for utility boilers such as low excess air firing and staged combustion may act to increase POM compound formation. The principle of these  $\text{NO}_x$  control techniques is to limit the oxygen available for  $\text{NO}_x$  formation in the combustion zone. Limiting oxygen effects a lower air/fuel ratio and may cause increased POM formation. Data to completely characterize the effect of combustion source  $\text{NO}_x$  controls on POM emissions are very limited and inconsistent (Mead et al., 1986; Kelly, 1983).

The most common SO<sub>2</sub> control technology currently used on utility boilers is lime/limestone flue gas desulfurization (FGD). This technology employs a wet scrubber for SO<sub>2</sub> removal and is often preceded by an ESP, which accomplishes the bulk of PM control. Wet FGD/ESP systems, while providing for the control of POM condensed on particulate matter at the entrance to the ESP, have been shown to poorly control vapor phase POM. Tests examining benzo(a)pyrene showed that condensation of the vapor phase POM compound would occur in the scrubber, but significant collection of POM particles remaining in the gas flow through the scrubber was not achieved (Mead et al., 1986; Kelly, 1983).

A more recently applied SO<sub>2</sub> control technique for utility boilers is spray drying. In this process, the gas stream is cooled in the spray dryer but remains above the saturation temperature. A fabric filter or an ESP is located downstream of the spray dryer, thus providing for significant control of both particulate and vapor phase POM because the vapor phase compounds are condensed before they reach the baghouse or ESP (Mead et al., 1986; Kelly, 1983).

In general, emissions of organic pollutants, including POM, are reduced by operating the furnace in such a way as to promote complete combustion of the fossil fuel(s) combusted in the furnace. Therefore, any combustion modification which increases the combustion efficiency will most likely reduce POM emissions.

#### Process Description--Industrial/Commercial Sector

Industrial boilers are widely used in manufacturing, processing, mining, and refining, primarily to generate process steam, electricity, or space heat at the facility. However, the industrial generation of electricity is limited, with only 10 to 15 percent of industrial boiler coal consumption and 5 to 10 percent industrial boiler gas and oil consumption used for electricity generation (U.S. EPA, 1982). Commercial boilers are used by commercial establishments, medical institutions, and educational institutions to provide space heating. In collecting survey data to support its Industrial Combustion Coordinated Rulemaking (ICCR), the EPA compiled information on a total of 69,494 combustion boiler units in the industrial and

commercial sectors (U.S. EPA, 1998). While this number likely underestimates the total population of boilers in the industrial and commercial sectors (due to unreceived survey responses and lack of information on very small units) it provides an indication of the large number of sources included in this category.

Of the units included in the ICCR survey database, approximately 70 percent were classified in the natural gas fuel subcategory, 23 percent in the oil (distillate and residual) subcategory, and 6 percent in the coal burning subcategory. These fuel subcategory assignments characterize the market population of boiler units according to their primary fuel burned, and are based on the units burning only greater than 90 percent of the specified fuel for that subcategory. All other units (accounting for the other 1 percent of assignments) are assigned to a subcategory of “other fossil fuel” (U.S. EPA, 1998).

Other fuels burned in industrial boilers are wood wastes, liquified petroleum gas, asphalt, and kerosene. Of these fuels, wood waste is the only non-fossil fuel discussed here, since POM emissions were not characterized for combustion of the other fuels. The burning of wood waste in boilers is mostly confined to those industries where it is available as a by-product. It is burned both to obtain heat energy and to alleviate possible solid waste disposal problems. Generally, bark is the major type of waste burned in pulp mills. In the lumber, furniture, and plywood industries, either a mixture of wood and bark waste or wood waste alone is most frequently burned. As of 1980, there were approximately 1,600 wood-fired boilers operating in the United States, with a total capacity of over 30,000 MW (U.S. EPA, 1994b).

Many of the same types of boilers used by the utility sector are also utilized by the industrial/commercial sector; however, the average boiler size used by the industrial/commercial sector is substantially smaller. Additionally, a few types of boiler designs are used only by the industrial/commercial sector. For a general description of the major subassemblies of and key thermal processes that occur in boilers, refer to Utility Sector process description and Figures 4.1.2-1 through 4.1.2-5.

Water-tube Boilers--In water-tube boilers, the water being heated flows through tubes surrounded by circulating hot gases. Water-tube boilers represent the majority (i.e., 57 percent) of industrial and commercial boiler capacity (70 percent of industrial boiler capacity) (U.S. EPA, 1982).

Water-tube boilers are used in a variety of applications ranging from supplying large amounts of process steam to providing space heat for industrial and commercial facilities. These boilers have capacities ranging from 2.9 MW to 439.5 MW, averaging about 120 MW. The most common types of water-tube boilers used in the industrial/commercial sector are wall-fired and stoker-fired boilers. Tangentially-fired and FBC boilers are less commonly used. Refer to Utility Sector for descriptions of these boiler designs (U.S. EPA, 1979).

Fire-tube and Cast Iron Boilers--The industrial/commercial sector also uses boilers with two other types of heat transfer methods: fire-tube and cast iron boilers. In fire-tube boilers, the hot gas flows through the tubes and the water being heated circulates outside of the tubes. Fire-tube boilers are not available with capacities as large as water-tube boilers, but they are also used to produce process steam and space heat. Most fire-tube boilers have a capacity 0.4 to 7.3 MW thermal. Most installed fire-tube boilers burn oil or gas and are used primarily in commercial/institutional applications (U.S. EPA, 1979).

In cast iron boilers, the hot gas is also contained inside the tubes that are surrounded by the water being heated, but the units are constructed of cast iron instead of steel. Cast iron boilers are limited in size and are used only to supply space heat. Cast iron boilers range in size from less than 0.1 to 2.9 MW thermal (U.S. EPA, 1979).

Wood Waste Boilers--The burning of wood waste in boilers is mostly confined to those industries where it is available as a by-product. Wood waste is burned both to obtain heat energy and to alleviate solid waste disposal problems. Wood waste may include large pieces such as slabs, logs, and bark strips, as well as cuttings, shavings, pellets, and sawdust (U.S. EPA, 1994b).

Various boiler firing configurations are used in burning wood waste. One common type in smaller operations is the dutch oven or extension type of furnace with a flat grate. This unit is widely used because it can burn fuels with very high moisture. Fuel is fed into

the oven through apertures in a firebox and is fired in a cone-shaped pile on a flat grate. The burning is done in two stages: (1) drying and gasification, and (2) combustion of gaseous products. The first stage takes place in a cell separated from the boiler section by a bridge wall. The combustion stage takes place in the main boiler section (U.S. EPA, 1994b).

In another type of boiler, the fuel-cell oven, fuel is dropped onto suspended fixed grates and is fired in a pile. The fuel cell uses combustion air preheating and positioning of secondary and tertiary air injection ports to improve boiler efficiency (U.S. EPA, 1994b).

In many large operations, more conventional boilers have been modified to burn wood waste. The units may include spreader stokers with traveling grates or vibrating grate stokers, as well as tangentially fired or cyclone-fired boilers (see Utility Sector for descriptions of these types of boilers). The most widely used of these configurations is the spreader stoker, which can burn dry or wet wood. Fuel is dropped in front of an air jet, which casts the fuel out over a moving grate. The burning is done in three stages: (1) drying, (2) distillation and burning of volatile matter, and (3) burning of fixed carbon. Natural gas or oil is often fired as auxiliary fuel. This is done to maintain constant steam when the wood supply fluctuates or to provide more steam than can be generated from the wood supply alone (U.S. EPA, 1994b).

Sander dust is often burned in various boiler types at plywood, particle board, and furniture plants. Sander dust contains fine wood particles with low moisture content (less than 20 percent by weight). It is fired in a flaming horizontal torch, usually with natural gas as an ignition aid or supplementary fuel (U.S. EPA, 1994b).

A recent development in wood-firing is the FBC boiler. Refer to Utility Sector for a description of this boiler-type. Because of the large thermal mass represented by the hot inert bed particles, FBCs can handle fuels with high moisture content (up to 70 percent, total basis). Fluidized beds can also handle dirty fuels (up to 30 percent inert material). Wood material is pyrolyzed faster in a fluidized bed than on a grate due to its immediate contact with hot bed material. As a result, combustion is rapid and results in nearly complete combustion of organic matter, thereby minimizing emission of unburned organic compounds (U.S. EPA, 1994b).

The composition of wood waste depends largely on the industry from which it originates and may have an impact on POM emissions. Pulping operations, for example, produce great quantities of bark that may contain more than 70 percent by weight moisture, along with sand and other noncombustibles. Because the high moisture content and the presence of noncombustibles inhibits complete combustion, bark boilers in pulp mills may emit considerable amounts of organic compounds to the atmosphere unless they are well controlled. On the other hand, some operations, such as furniture manufacturing, produce a clean, dry wood waste, 5 to 50 percent by weight moisture, with relatively low organic emissions when properly burned. Still other operations, such as sawmills, burn a varying mixture of bark and wood waste that results in particulate emissions somewhere between those of pulp mills and furniture manufacturing. Additionally, when fossil fuels are co-fired with wood waste, the combustion efficiency is typically improved; therefore, organic emissions may decrease (U.S. EPA, 1997).

The ratio of overfire to underfire air also plays an important role in organic emissions. Based on test results, it has been speculated that if the balance of combustion air heavily favors underfire air, there is insufficient combustion air in the upper furnace to complete the combustion of the products of incomplete combustion (PICs) (including POM). Conversely, with excessive overfire air, the flame quenching effect of too much combustion air in the upper furnace appears to suppress the combustion of the PICs at that stage of the combustion process (Hubbard, 1991).

Waste Oil Combustion--Waste oil is another type of fuel that is burned primarily in small industrial/commercial boilers and space heaters. Space heaters are small combustion units (generally less than 250,000 Btu/hr [0.1 MW] heat input) that are common in automobile service stations and automotive repair shops where supplies of waste crankcase oil are available (U.S. EPA, 1995c).

Waste oil includes used crankcase oils from automobiles and trucks, used industrial lubricating oils such as metal working oils, and other used industrial oils such as heat transfer fluids. When discarded, these oils become waste oils due to a breakdown of physical properties and to contamination by other materials. The different types of waste oils may be

burned as mixtures or as single fuels where supplies allow. Boilers designed to burn No. 6 (residual) fuel oils or one of the distillate fuel oils can be used to burn waste oil, with or without modifications for optimizing combustion. As an alternative to boiler modification, the properties of waste oil can be modified by blending it with fuel oil, to the extent required to achieve a clean-burning fuel mixture.

Emission Control Techniques--POM emissions from industrial/commercial boilers may be dependent on various factors, including: (1) the type of fuel burned, (2) the type of boiler used, (3) operation conditions of the boiler, and (4) pollution control device(s) used. Conditions that favor more complete combustion of the fuel generally result in lower organic emissions. Additionally, the organic emission potential of wood combustion is generally thought to be greater than that of fossil fuel combustion because wood waste has a lower heating value and higher moisture content, which may decrease combustion efficiency.

The type of boiler, as well as its operation, affects combustion efficiency and emissions. Wood-fired boilers require a sufficiently large refractory surface to ensure proper drying of high-moisture-content wood waste prior to combustion. Adequately dried fuel is necessary to avoid a decrease in combustion temperatures, which may increase organic emissions because of incomplete combustion (U.S. EPA, 1997). Flyash reinjection, which is commonly used in large wood-fired boilers to improve fuel efficiency, may increase PM and particulate POM emissions. The process involves the reinjection of multicyclone collected flyash to the boiler, thus increasing PM loading to air emission control device(s). In modern flyash reinjection boiler installations, the collected flyash is segregated into large and small sizes via sand classifiers before reinjection of the large carbonaceous particles and disposal of the smaller, mostly inorganic fraction (U.S. EPA, 1995a).

Emission controls for industrial boilers and their effect on POM emissions are very similar to those previously described for utility boilers. Particulate matter control in the industrial sector is being achieved by the use of baghouses, ESPs, wet scrubbers, and multicyclones. For SO<sub>2</sub> control, FGD systems are much less frequent in the industrial sector as

opposed to the utility sector; however, they are used. Generally, in the industrial sector, SO<sub>2</sub> regulations are met through the burning of lower sulfur content fuels (Mead et al., 1986; Kelly, 1983).

Particulate matter emissions from oil-fired industrial boilers are generally not controlled under existing regulations because emission rates are low relative to coal-fired sources. Some areas may limit SO<sub>2</sub> emissions from oil firing by specifying the use of lower sulfur content oils. Natural gas industrial boilers are generally uncontrolled because of very low emissions PM and SO<sub>2</sub> relative to coal and oil sources (Mead et al., 1986; Kelly, 1983).

Wood-fired industrial boilers are typically controlled by multicyclones followed by venturi or impingement-type wet scrubbers for PM control. A limited number of wood-fired boiler installations use ESPs for PM control. The effect of both of these control systems on POM emissions reduction is estimated to be similar to that obtained at coal-fired units using the same technology (i.e., potentially good particulate and vaporous POM control with scrubbers and effective particulate POM, but no vaporous POM control with ESPs). Bagasse-fired boilers are also controlled with predominantly wet scrubbers and, to a lesser extent, multicyclones (Mead et al., 1986; Kelly, 1983).

Unless the facilities are unusually large, emissions control at commercial/institutional sources is marginal or even nonexistent. In boilers with controls, the control system generally only consists of multicyclones. Multicyclones would effect some control on larger particulate POM, but would have no control impact on fine particulate POM and gaseous POM compounds (Mead et al., 1986; Kelly, 1983).

#### Emission Factors

Extensive POM emissions data for utility, industrial and commercial stationary external combustion sources are available in the technical literature. Because of their propensity to form and release POM emissions and the applicability of State and Federal air pollution



regulations which often require testing for emissions of toxic air pollutants, a significant current database of emissions from these fuel combustion sources exists.

Emission factors for utility, industrial and commercial stationary external combustion source categories are presented in Tables 4.1.2-1 to 4.1.2-13 and discussed under the following sub-headings:

- Wood waste combustion;
- Wood waste-fired industrial boilers;
- Natural gas-fired utility boilers;
- Natural gas-fired industrial and commercial/institutional boilers;
- Anthracite coal combustion;
- Coal-fired utility boilers;
- Coal-fired industrial and commercial/institutional boilers;
- Oil-fired boilers;
- Oil-fired industrial process heaters;
- Waste oil-fired space heaters; and
- Bagasse combustion.

Wood Waste Combustion--General PAH emission factors for uncontrolled wood waste combustion in utility, industrial and commercial boilers are presented in Table 4.1.2-1. The emission factor units are lb (kg) per ton (Mg) of wood waste combusted on an as fired basis of 50 percent moisture and 4,500 Btu/lb (2,500 kcal/kg). U.S. EPA (1995a) reports these emission factors as widely applicable to all utility, industrial and commercial wood waste combustion SCC categories. However, due to the wide range of boiler sizes, boiler and control device configurations and fuel characteristics represented by these composite emission factors, it is

recommended that the reader utilize the process specific emission factors presented below if information exists to more accurately characterize the emission source.

Wood Waste-Fired Industrial Boilers--Average emission factors for industrial wood waste-fired boilers are presented in Table 4.1.2-2. The emission factors are based on two comprehensive toxic air emission testing programs involving facilities in California and North Carolina. The summarized results of both studies were used to obtain the average PAH emission factors and emission factor ranges in Table 4.1.2-2. The emission factors are representative of a range of boiler designs and capacities, control configurations and wood waste composition.

In one study, conducted by the Timber Association of California (TAC), 11 boilers ranging from 6 to 167 lb (13 to 368 kg) of steam per hour were tested. Five boiler types were included in the testing program: fuel cell, dutch oven, stoker, air injection and fluidized bed. The range of control devices represented in the sample set included cyclones, multicyclones, ESPs and wet scrubbers. Sampling was conducted using CARB Method 429, which captures both vapor phase and particulate PAHs (Sassenrath, 1991).

In another study, test data from seven industrial wood waste-fired boilers in North Carolina were summarized. Tested units included horizontal four return tube (HRT) boilers, one underfeed stoker, one watertube boiler and one fluidized bed boiler. The rated capacity range of the tested units was 5 to 70 MMBtu/hr (1.5 to 20.5 MW). Four of the tested units used multicyclones for air emission control and three were uncontrolled. Wood waste fuel types fired during testing included green and dry hardwood and softwood wood waste and bark. Sampling was conducted using EPA Modified Method 5, which captures both vapor phase and particulate POM, followed by GC analysis (NCASI, 1983; Sassenrath, 1991).

Naphthalene was the predominant PAH detected in both studies followed by phenanthrene, fluorene and pyrene. Sassenrath (1991) concluded from the TAC study that PAH emissions from properly operated modern wood waste-fired boilers were low relative to earlier estimates and very low relative to less efficient residential wood combustion. Benzo(a)pyrene was only detected in one sample of the test series.

Table 4.1.2-3 presents PAH emission factors for bark-fired industrial boilers. A single spreader stoker operating at 131,500 to 138,900 lb (59,648 to 63,005 kg) of steam per hour was tested. The boiler was firing redwood and fir bark during testing. Sampling for PAHs was conducted using CARB Method 429. The emission factors represent both vapor phase and particulate PAHs.

Table 4.1.2-4 lists PAH emission factors for wood waste-fired industrial boilers of greater than 50,000 lb (22,680 kg) of steam per hour capacity. Emission factors for several specific boiler designs, capacities, fuel types and control device configurations are presented. All emission factors represent both vapor phase and particulate PAHs. The table contains PAH emission factors for the following boiler and control device scenarios: a dutch oven wood waste boiler controlled by multicyclone, a fuel cell boiler controlled by multicyclone, an air injection burner controlled by multicyclone, three stokers, two controlled by multicyclone and wet scrubber in series and one controlled by multicyclone and ESP in series and one fluidized bed wood waste boiler controlled by multicyclone and ESP in series. Where available, the operating load during testing in lb (kg) of steam per hour and the specific fuel source are footnoted in the table.

PAH emission factors for wood waste-fired industrial boilers less than 50,000 lb (22,680 kg) of steam per hour capacity are presented in Table 4.1.2-5. Two units were tested, one cyclone-controlled fuel cell firing fir sawdust fuel and one boiler of unknown design controlled with a wet scrubber firing cedar chips. The steaming rate range represented in the test data was 6,400 to 34,000 lb (2,903 to 15,422 kg) of steam per hour. Sampling and analytical methods were used to quantify both vapor phase and particulate PAHs.

Natural Gas-Fired Utility Boilers--PAH emission factors for natural gas-fired utility boilers are listed in Table 4.1.2-6. The emission factors are based on test data from two opposed-fired natural gas-fired utility boilers, one uncontrolled and one with flue gas recirculation. The uncontrolled utility boiler was a 2,561 MMBtu/hr (750 MW) unit. Sampling was conducted using CARB Method 429 followed by GC/MS analysis. The 16 commonly tested PAHs were analyzed in the study, but only three, anthracene, naphthalene, and phenanthrene, were

determined to be present above the detection limits in any sample (Booth, 1992). The second unit tested was a 785 MMBtu/hr (230 MW) utility boiler with flue gas recirculation. Stack gases from this unit were sampled using CARB Method 430 at three operating loads, 109 MW, 159 MW and 222 MW. Both sets of emission factors represent both vapor phase and particulate PAHs. Naphthalene was the predominant PAH detected in the emissions from both units.

Natural Gas-Fired Industrial and Commercial/Institutional Boilers--PAH emission factors for industrial and commercial/institutional boilers are presented in Table 4.1.2-7. The industrial natural gas-fired boiler emission factors are composite factors based on 10 uncontrolled units. The following boiler designs were included in the emissions database: two fire-tube, one scotch, and seven water-tube. The sample included a rated capacity range of 7.2 to 178 MMBtu/hr (2.1 to 52 MW). The commercial/institutional boiler emission factors are based on data from five tested uncontrolled packaged watertube boilers ranging in capacity from 17.4 to 126 MMBtu/hr (5.1 to 37 MW). Sampling for both data sets was conducted using the Source Assessment Sampling System (SASS). The system was designed to trap particulate and gases from the flue gas stream, separating particulate and adsorbing organics on XAD-2 resin. The particulate and vapor phase PAHs were then analyzed using GC/MS. As in the utility boiler data, naphthalene was the predominant PAH detected in the emissions from natural gas-fired industrial and commercial/institutional boilers (Johnson et al., 1990; Surprenant et al., 1981).

Anthracite Coal Combustion--PAH emission factors for anthracite coal combustion are listed in Table 4.1.2-8. According to U.S. EPA (1995a) the emission factors are applicable to uncontrolled utility, industrial and commercial/institutional stoker anthracite combustion. However, the factors are based on test data from three commercial/institutional stoker boilers, and thus, may have limited applicability in predicting PAH emissions from large modern utility and industrial boilers. The tested units had a rated capacity range of 8.7 to 87 MMBtu/hr (2.5 to 25 MW). Only two of the 16 commonly tested PAHs, naphthalene and phenanthrene, were detected in the analysis of samples from the three tested boilers. The reported emission factors represent both vapor phase and particulate PAHs.

Coal-Fired Utility Boilers--PAH emission factors for bituminous and lignite coal-fired utility boilers are presented in Table 4.1.2-9. The table includes composite emission factors for bituminous pulverized wet-bottom boilers, bituminous pulverized dry-bottom boilers, and lignite-fired boilers. The pulverized wet-bottom boiler average emission factors are based on six tested utility boilers with a rated capacity range of 376 to 2,834 MMBtu/hr (110 to 830 MW). The pulverized dry-bottom boiler average emission factors are based on test data from six boilers with a rated capacity range of 263 to 1,707 MMBtu/hr (77 to 500 MW). The lignite-fired boiler composite emission factors are based on nine tested utility boilers, five pulverized dry-bottom boilers, two cyclones and two spreader stokers with a rated capacity range of 68 to 1,434 MMBtu/hr (20 to 420 MW). All three sets of composite emission factors represent units with a range of common control configurations including multicyclones, ESPs and scrubbers. The emission factors include both vapor phase and particulate PAHs (Johnson et al., 1990; Shih et al., 1980).

In addition to these composite emission factors, three source/control specific emission factor sets are presented. These include a bituminous coal-fired cyclone boiler equipped with an ESP, a bituminous coal-fired cyclone boiler equipped with a baghouse and a combined SO<sub>2</sub> and NO<sub>x</sub> control system (SNOX) and a pulverized lignite-fired tangential dry-bottom boiler equipped with an ESP and wet FGD (Sverdrup et al., 1994). Information on the specific boilers used in emission factor development, including operating rates and control devices is presented in footnotes to the emission factor sets in Table 4.1.2-10. All emission factors represent both vapor phase and particulate PAH emissions.

Coal-Fired Industrial and Commercial/Institutional Boilers--PAH emission factors for coal-fired industrial and commercial/institutional boilers are listed in Table 4.1.2-10. Composite emission factors for two industrial boiler design categories, pulverized bituminous coal-fired wet and dry-bottom boilers and bituminous stokers, are presented. The pulverized bituminous coal-fired industrial boiler emission factors are based on test data from seven units, both wet and dry-bottom, with a rated capacity range of 116 to 1,261 MMBtu/hr (34 to 366 MW). Five of the seven units were multicyclone controlled, three were ESP controlled and one unit had a FGD system. Test data from 17 bituminous coal-fired stokers was used in deriving composite PAH

emission factors for this design category. The sample set included 11 spreader stokers, five overfeed stokers and one underfeed stoker. Control configurations included uncontrolled, multicyclone controlled and ESP controlled. Both PAH emission factor sets represent both vapor phase and particulate emissions (Johnson et al., 1990; Shih et al., 1980).

The PAH emission factor set for coal-fired commercial/institutional boilers is based on testing from a single uncontrolled bituminous coal-fired underfeed stoker. The rated capacity of the boiler was 2.2 MMBtu/hr (0.63 MW). During testing, the boiler was operated at low heat input levels, possibly contributing to the relatively high POM emissions. The reported emission factors include both vapor phase and particulate PAHs (Johnson et al., 1990; Shih et al., 1980).

Oil-Fired Boilers--PAH emission factors for oil-fired utility, industrial and commercial/institutional boilers are presented in Table 4.1.2-11. Emission factor ranges from multiple uncontrolled residual oil-fired utility boilers were presented by Booth (1992). The test data used to develop the PAH emission factor ranges were compiled from CARB AB-2588 facility emissions test reports. Boiler designs included in the database included front- and opposed-fired boilers with a rated capacity range of 188 to 2,523 MMBtu/hr (55 to 739 MW). Sampling for all test data was conducted using CARB Method 429 followed by GC/MS analysis. Both vapor phase and particulate PAHs are included in the emission factors. Booth (1992) noted that naphthalene, the predominant PAH identified in the study, was a decomposition product of the XAD-2 resin used in the CARB Method 429 sampling protocol, possibly raising questions about the validity of the naphthalene emissions estimates. Insufficient data were available in the study to calculate average emission factors; however, median emission factors may be used for general application if information is not available to further characterize the emissions source.

Emission factors for three specific utility boiler and control configurations are listed in Table 4.1.2-12. The three boilers tested were a No. 6 oil wall-fired uncontrolled utility boiler, a No. 6 oil wall-fired utility boiler with flue gas recirculation and a No. 5 oil-fired utility boiler with flue gas recirculation. The boiler rated capacities were 598 MMBtu/hr (1,75 MW), 1,639 MMBtu/hr (480 MW) and 785 MMBtu/hr (230 MW), respectively. Sampling for all three

data sets was conducted using CARB Method 429 followed by GC/MS analysis. The emission factors represent both vapor phase and particulate PAHs.

PAH emission factors for No. 6 oil-fired industrial boilers are presented in Table 4.1.2-12. The data used in factor development came from testing of a single uncontrolled unit. Testing was conducted using CARB Method 429 followed by GC/MS analysis. The emission factors represent both vapor phase and particulate PAHs.

PAH emission factors for No. 2 oil-fired industrial and commercial/institutional boilers are also listed in Table 4.1.2-12. The average emission factors are based on eight tested units. Included in the data set were five water-tube industrial boilers with a rated capacity range of 23 to 529 MMBtu/hr (6.7 to 155 MW) and three commercial/institutional boilers, one cast iron and two water-tube, with a rated capacity range of 5 to 35 MMBtu/hr (1.5 to 10.3 MW). Test methods were used to quantify both particulate and vapor phase POM. PAH emissions were reported as being below detection limits for several of the tested units (Johnson et al., 1990; Surprenant et al., 1980).

Oil-Fired Industrial Process Heaters--PAH emission factors for oil-fired industrial process heaters are presented in Table 4.1.2-12. The emission factors were developed using test data from a single 20,800 Btu/hr (6,092 MW) direct fire pipeline fuel oil heater firing residual oil. PAH emissions sampling and analytical methods used were CARB Method 429 and GC/MS, respectively. Emission factors represent both vapor phase and particulate PAHs.

Waste Oil-Fired Space Heaters--PAH emission factors for waste oil combustion are shown in Table 4.1.2-13. Emission factors have been determined for emissions from two basic types of uncontrolled space heaters: a vaporizing pot type burner and an air atomizing burner. The use of both blended and unblended fuels is included in the factors that were obtained from U.S. EPA (1995c). The factors obtained from Cooke et al. (1984), are based on the combustion of filtered, but otherwise untreated waste crankcase oil from automobiles. Both sets of factors are based on samples of stack effluent from waste oil heaters rated at less than 0.1 MW.

The vaporized pot design showed higher emissions of PAH than did the atomizing burner space heater. In a vaporized pot burner only the heater vaporized fuel is combusted. In the air atomizing burner the fuel is atomized and then burned, resulting in much less residue of unburned material than the vaporized pot burner. Cooke et al. (1984), reported that the combustion of waste oil in the vaporized pot burner that they tested resulted in higher PAH emissions than those reported for residential space heaters burning distillate oil.

Bagasse Combustion--Very limited data on emissions from bagasse combustion in boilers were available in the literature. One test report quantified total particulate and vapor phase POM emissions from two industrial bagasse-fired boilers in Hawaii (Baladi, 1976). The study reported total POM emissions from multicyclone controlled bagasse-fired boilers of  $4.00\text{E-}5$  to  $1.80\text{E-}4$  lb/MMBtu ( $1.72\text{E-}5$  to  $7.75\text{E-}5$  g/MJ). The limited speciation data reported in the study indicated that none of the 16 commonly investigated PAHs were present above detection limits in the samples. The predominant POM compounds measured were 3-methylcholanthrene and 7,12-dimethyl-benz(a)anthracene. Due to the age of the data and the limited speciation of the total POM measured, individual PAH emission factors were not developed for this source category.

#### Source Locations

Most of the U.S. utility coal-firing capability is east of the Mississippi River, with the significant remainder being in the Rocky Mountain region. Natural gas is used primarily in the South Central States and California. Oil is predominantly used in Florida and the Northeast. Fuel economics and environmental regulations affect regional use patterns. For example, coal is not used in California because of stringent air quality limitations. Information on precise utility plant locations can be obtained by contacting utility trade associations such as the Electric Power Research Institute in Palo Alto, California (415-855-2000); the Edison Electric Institute in Washington, DC (202-828-7400); or the U.S. Department of Energy (DOE) in Washington, DC.

Industrial and commercial coal combustion sources are located throughout the United States, but tend to follow industry and population trends. Most of the coal-fired industrial



boiler sources are located in the Midwest, Appalachian, and Southeast regions. Industrial wood-fired boilers tend to be located almost exclusively at pulp and paper, lumber products, and furniture industry facilities. These industries are concentrated in the Southeast, Gulf Coast, Appalachian, and Pacific Northwest regions.

Trade associations such as the American Boiler Manufacturers Association in Arlington, Virginia (703-522-7350) and the Council of Industrial Boiler Owners in Fairfax Station, Virginia (703-250-9042) can provide information on industrial boiler locations and trends (U.S. EPA, 1997).

TABLE 4.1.2-1. PAH EMISSION FACTORS FOR WOOD WASTE COMBUSTION

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
1-01-009-01, -02, -03, -04, -05, -06, -07	Wood Waste Fired Boiler	None	Benz(a)anthracene	1.8E-06 (9.0E-07)	8.6E-8 - 6.4E-6 (4.3E-8 - 3.2E-6)	C
			Benzo(a)pyrene	1.9E-07 (9.5E-08)	8.6E-8 - 3.0E-7 (4.3E-8 - 1.5E-7)	D
			Benzo(b+k)fluoranthene	2.9E-05 (1.5E-05)	3.4E-7 - 1.9E-4 (1.7E-7 - 9.5E-5)	C
			Chrysene	4.3E-05 (2.1E-05)	8.6E-8 - 3.0E-4 (4.3E-8 - 1.5E-4)	C
			Indeno(1,2,3-cd)pyrene	3.4E-07 (1.7E-07)	8.6E-8 - 6.0E-7 (4.3E-8 - 3.0E-7)	D
			Acenaphthene	3.4E-06 (1.7E-06)	8.6E-8 - 4.3E-6 (4.3E-8 - 2.1E-6)	C
			Acenaphthylene	4.4E-05 (2.2E-05)	6.0E-7 - 6.8E-5 (3.0E-7 - 3.4E-5)	C
			Anthracene	3.8E-05 (1.9E-05)	8.6E-8 - 3.5E-4 (4.3E-8 - 1.7E-4)	C
			Benzo(ghi)perylene	1.2E-06 (6.0E-07)	8.6E-8 - 3.5E-6 (4.3E-8 - 1.7E-6)	C
			Fluoranthene	9.0E-05 (4.5E-05)	8.6E-8 - 8.6E-4 (4.3E-8 - 4.3E-4)	C
			Fluorene	9.6E-06 (4.8E-06)	1.7E-7 - 2.8E-5 (8.5E-8 - 1.4E-5)	C

(continued)

TABLE 4.1.2-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
1-01-009-01, -02, -03, -04, -05, -06, -07 (continued)	Wood Waste Fired Boiler (continued)	None	Naphthalene	2.3E-03 (1.1E-03)	5.0E-5 - 5.8E-3 (2.5E-5 - 2.9E-3)	C
			Phenanthrene	5.7E-05 (2.8E-05)	2.0E-6 - 1.8E-4 (1.0E-6 - 9.0E-5)	C
			Pyrene	1.7E-05 (8.5E-06)	4.3E-7 - 5.9E-5 (2.1E-7 - 2.9E-5)	C
			Methyl anthracene	1.4E-04 (7.00E-05)	---	D

<sup>a</sup>Emission factors are in lb (kg) per ton (Mg) of wood waste burned. Emission factors are based on wet, as fired wood waste with average properties of 50 percent moisture and 4,500 Btu/lb higher heating value.

Source: U.S. EPA, 1995a.

TABLE 4.1.2-2. PAH EMISSION FACTORS FOR INDUSTRIAL WOOD WASTE BOILERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>b</sup>	Emission Factor Rating
1-02-009-01, -02, -03, -04, -05, -06	Wood Waste Fired Boiler <sup>c</sup>	(d)	Benz(a)anthracene	<2.70E-05 (1.35E-05)	<2.0E-6 - 5.2E-5 (1.0E-6 - 2.6E-5)	C
			Benzo(a)pyrene	7.01E-06 (3.50E-06)	2.0E-8 - 1.4E-5 (1.0E-8 - 7.0E-6)	C
			Benzo(b+k)fluoranthene	<1.10E-05 (5.50E-06)	<2.0E-6 - 2.0E-5 (1.0E-6 - 1.0E-5)	C
			Chrysene	<9.00E-06 (4.50E-06)	<2.0E-6 - 1.6E-5 (1.0E-6 - 8.0E-6)	C
			Dibenz(a,h)anthracene	2.00E-06 (1.00E-06)	0.0 - 4.0E-6 (0.0 - 2.0E-6)	C
			Indeno(1,2,3-cd)pyrene	3.00E-06 (1.50E-06)	<2.0E-6 - 4.0E-6 (1.0E-6 - 2.0E-6)	C
			Acenaphthene	<2.00E-06 (1.00E-06) <sup>e</sup>	---	C
			Acenaphthylene	7.20E-05 (3.60E-05) <sup>e</sup>	---	C
			Anthracene	6.60E-05 (3.30E-05)	4.0E-6 - 1.28E-4 (2.0E-6 - 6.4E-5)	C
			Benzo(ghi)perylene	<7.00E-06 (3.50E-06)	<2.0E-6 - 1.2E-5 (1.0E-6 - 6.0E-6)	C
			Fluoranthene	2.50E-05 (1.25E-05)	1.4E-5 - 3.6E-5 (7.0E-6 - 1.8E-5)	C

(continued)

TABLE 4.1.2-2. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>b</sup>	Emission Factor Rating
1-02-009-01, -02, -03, -04, -05, -06 (continued)	Wood Waste Fired Boiler <sup>c</sup> (continued)	(d)	Fluorene	5.70E-05 (2.85E-05)	1.2E-5 - 1.02E-4 (6.0E-6 - 5.1E-5)	C
			Naphthalene	0.00288 (0.00144)	0.00263 - 0.00313 (0.00131 - 0.00156)	C
			Phenanthrene	1.51E-04 (7.55E-05)	8.6E-5 - 2.16E-4 (4.3E-5 - 1.08E-4)	C
			Pyrene	4.20E-05 (2.10E-05)	3.4E-5 - 5.0E-5 (1.7E-5 - 2.5E-5)	C

<sup>a</sup>Emission factors are in lb (kg) per ton (Mg) of wood waste burned (moisture conditions as fired).

<sup>b</sup>Emission factor range represents range between two sets of summarized emission factors. Emission factor set No. 1 is the mean of 11 tested boilers by the Timber Association of California. Emission factor set No. 2 is the mean of 7 boilers tested in North Carolina by the National Council of the Paper Industry for Air and Stream Improvement (NCASI).

<sup>c</sup>Includes test data from several boiler designs including stoker, dutch oven, fuel cell, and fluidized bed.

<sup>d</sup>Includes test data from several boiler air emission control systems including multiple cyclones, ESPs, and scrubbers.

<sup>e</sup>Pollutants not measured in NCASI Study.

Source: Sassenrath, 1991.

TABLE 4.1.2-3. PAH EMISSION FACTORS FOR BARK-FIRED INDUSTRIAL BOILERS

SCC Number	Emission Source <sup>b</sup>	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating
1-02-009-01	Stoker	Multiple Cyclone/Electrostatic Precipitator	Acenaphthene	<1.5E-08 (6.4E-09)	D
			Acenaphthylene	7.4E-06 (3.2E-06)	D
			Anthracene	<1.9E-07 (8.2E-08)	D
			Fluoranthene	2.1E-06 (9.0E-07)	D
			Fluorene	2.0E-07 (8.6E-08)	D
			Phenanthrene	6.8E-06 (2.9E-06)	D
			Pyrene	1.2E-06 (5.2E-07)	D

<sup>a</sup>Emission factors are in lb (g) of pollutant per MMBtu (MJ) of heat input.

<sup>b</sup>Emission source: Spreader stoker operated at 131,500 to 138,900 lb (59,648 to 63,005 kg) steam/hr firing redwood and fir bark.

Source: Source Emission Testing of the Wood-fired Boiler "C" Exhaust at Pacific Timber, Scotia, California. Performed for the Timber Association of California. Galston Technical Services, February 1991.

TABLE 4.1.2-4. PAH EMISSION FACTORS FOR WOOD WASTE-FIRED INDUSTRIAL BOILERS >50,000 LB STEAM/HR

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-009-03	Dutch Oven <sup>b</sup>	Multiple Cyclone <sup>c</sup>	Benzo(k)fluoranthene	<1.50E-07 (<6.45E-08)	---	D	FIRE <sup>j</sup>
			Acenaphthene	<1.20E-07 (<5.16E-08)	---	D	FIRE <sup>j</sup>
			Acenaphthylene	<3.80E-06 (<1.63E-06)	---	D	FIRE <sup>j</sup>
			Anthracene	<1.40E-07 (<6.02E-08)	---	D	FIRE <sup>j</sup>
			Benzo(ghi)perylene	6.00E-08 (2.58E-08)	---	D	FIRE <sup>j</sup>
			Fluoranthene	9.60E-07 (4.13E-07)	---	D	FIRE <sup>j</sup>
			Fluorene	<7.00E-08 (<3.01E-08)	---	D	FIRE <sup>j</sup>
			Naphthalene	d	---		FIRE <sup>j</sup>
			Phenanthrene	2.10E-06 (9.03E-07)	---	D	FIRE <sup>j</sup>
			Pyrene	1.30E-06 (5.59E-07)	---	D	FIRE <sup>j</sup>
1-02-009-03	Fuel Cell	Multiple Cyclone <sup>c</sup>	Benzo(a)pyrene	<7.50E-09 (<3.22E-09)	---	D	FIRE <sup>k</sup>
			Chrysene	5.40E-08 (2.32E-08)	---	D	FIRE <sup>k</sup>
			Indeno(1,2,3-cd)pyrene	<1.20E-08 (<5.16E-09)	---	D	FIRE <sup>k</sup>

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(continued)

TABLE 4.1.2-4. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-009-03 (continued)	Fuel Cell (continued)	Multiple Cyclone <sup>c</sup> (continued)	Acenaphthene	<6.50E-09 (<2.79E-09)	---	D	FIRE <sup>k</sup>
			Acenaphthylene	2.80E-07 (1.20E-07)	---	D	FIRE <sup>k</sup>
			Anthracene	<1.30E-08 (<5.59E-09)	---	D	FIRE <sup>k</sup>
			Benzo(ghi)perylene	<1.10E-08 (<4.73E-09)	---	D	FIRE <sup>k</sup>
			Fluoranthene	4.00E-07 (1.72E-07)	---	D	FIRE <sup>k</sup>
			Fluorene	<3.10E-08 (<1.33E-08)	---	D	FIRE <sup>k</sup>
			Naphthalene	<sup>d</sup>	---	D	FIRE <sup>k</sup>
			Phenanthrene	4.30E-07 (1.85E-07)	---	D	FIRE <sup>k</sup>
			Pyrene	2.40E-07 (1.03E-07)	---	D	FIRE <sup>k</sup>
1-02-009-03	Air Injection Burner <sup>e</sup>	Multiple Cyclone <sup>c</sup>	Benz(a)anthracene	4.20E-08 (1.81E-08)	---	D	FIRE <sup>l</sup>
			Chrysene	1.20E-07 (5.16E-08)	---	D	FIRE <sup>l</sup>
			Indeno(1,2,3-cd)pyrene	6.80E-08 (2.92E-08)	---	D	FIRE <sup>l</sup>



TABLE 4.1.2-4. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-009-03 (continued)	Air Injection Burner <sup>e</sup> (continued)	Multiple Cyclone <sup>c</sup> (continued)	Acenaphthene	4.90E-07 (2.11E-07)	---	D	FIRE <sup>l</sup>
			Acenaphthylene	5.00E-06 (2.15E-06)	---	D	FIRE <sup>l</sup>
			Anthracene	2.70E-07 (1.16E-07)	---	D	FIRE <sup>l</sup>
			Benzo(ghi)perylene	4.00E-07 (1.72E-07)	---	D	FIRE <sup>l</sup>
			Fluoranthene	4.90E-06 (2.11E-06)	---	D	FIRE <sup>l</sup>
			Fluorene	1.30E-07 (5.59E-08)	---	D	FIRE <sup>l</sup>
			Naphthalene	d	---	D	FIRE <sup>l</sup>
			Phenanthrene	6.00E-06 (2.58E-06)	---	D	FIRE <sup>l</sup>
			Pyrene	6.40E-06 (2.75E-06)	---	D	FIRE <sup>l</sup>
1-02-009-03	Stoker <sup>f</sup>	Multiple Cyclone/ Electrostatic Precipitator <sup>c</sup>	Acenaphthylene	4.80E-07 (2.06E-07)	---	D	FIRE <sup>m</sup>
			Fluoranthene	<1.98E-08 (<8.49E-09)	<6.50E-9 - 3.30E-8 (<2.79E-9 - 1.42E-8)	C	FIRE <sup>m,n</sup>
			Naphthalene	2.00E-04 (8.60E-05)	1.20E-4 - 2.80E-4 (5.16E-5 - 1.20E-4)	C	FIRE <sup>m,n</sup>

(continued)

TABLE 4.1.2-4. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-009-03 (continued)	Stoker <sup>f</sup> (continued)	Multiple Cyclone/ Electrostatic Precipitator <sup>c</sup> (continued)	Phenanthrene	1.70E-07 (7.31E-08)	---	D	FIRE <sup>m</sup>
			Pyrene	4.30E-08 (1.85E-08)	---	D	FIRE <sup>m</sup>
1-02-009-03	Fluidized Bed <sup>g</sup>	Multiple Cyclone/ Electrostatic Precipitator <sup>c</sup>	Benz(a)anthracene	<7.60E-09 (<3.27E-09)	---	D	FIRE <sup>o</sup>
			Chrysene	2.00E-08 (8.60E-09)	---	D	FIRE <sup>o</sup>
			Acenaphthylene	7.50E-08 (3.22E-08)	---	D	FIRE <sup>o</sup>
			Fluoranthene	2.20E-07 (9.46E-08)	---	D	FIRE <sup>o</sup>
			Fluorene	<2.50E-08 (<1.07E-08)	---	D	FIRE <sup>o</sup>
			Naphthalene	<6.60E-04 (<2.84E-04)	---	D	FIRE <sup>o</sup>
			Phenanthrene	4.90E-07 (2.11E-07)	---	D	FIRE <sup>o</sup>

TABLE 4.1.2-4. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-009-03 (continued)	Fluidized Bed <sup>g</sup> (continued)	Multiple Cyclone/ Electrostatic Precipitator <sup>c</sup> (continued)	Pyrene	5.10E-08 (2.19E-08)	---	D	FIRE <sup>o</sup>
1-02-009-03	Stoker <sup>h</sup>	Multiple Cyclone/ Wet Scrubber <sup>c</sup>	Benz(a)anthracene	<5.30E-09 (<2.28E-09)	---	D	FIRE <sup>p</sup>
			Benzo(k)fluoranthene	<2.00E-08 (<8.60E-09)	---	D	FIRE <sup>p</sup>
			Chrysene	<6.70E-09 (<2.88E-09)	---	D	FIRE <sup>p</sup>
			Acenaphthene	1.00E-07 (4.30E-08)	---	D	FIRE <sup>p</sup>
			Acenaphthylene	3.10E-07 (1.33E-07)	---	D	FIRE <sup>p</sup>
			Anthracene	2.10E-08 (9.03E-09)	---	D	FIRE <sup>p</sup>
			Fluoranthene	8.20E-08 (3.53E-08)	---	D	FIRE <sup>p</sup>
			Fluorene	5.50E-08 (2.36E-08)	---	D	FIRE <sup>p</sup>
			Naphthalene	<5.20E-04 (<2.24E-04)	---	D	FIRE <sup>p</sup>

TABLE 4.1.2-4. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-009-03 (continued)	Stoker <sup>h</sup> (continued)	Multiple Cyclone/ Wet Scrubber <sup>c</sup> (continued)	Phenanthrene	2.30E-07 (9.89E-08)	---	D	FIRE <sup>p</sup>
			Pyrene	9.60E-08 (4.13E-08)	---	D	FIRE <sup>p</sup>
1-02-009-03	Stoker <sup>i</sup>	Multiple Cyclone/ Wet Scrubber <sup>c</sup>	Benz(a)anthracene	<1.40E-06 (<6.02E-07)	---	D	FIRE <sup>q</sup>
			Acenaphthene	2.00E-06 (8.60E-07)	---	D	FIRE <sup>q</sup>
			Acenaphthylene	2.50E-05 (1.07E-05)	---	D	FIRE <sup>q</sup>
			Anthracene	1.80E-06 (7.74E-07)	---	D	FIRE <sup>q</sup>
			Fluoranthene	1.10E-05 (4.73E-06)	---	D	FIRE <sup>q</sup>
			Fluorene	5.80E-06 (2.49E-06)	---	D	FIRE <sup>q</sup>
			Naphthalene	<1.90E-04 (8.17E-05)	---	D	FIRE <sup>q</sup>

TABLE 4.1.2-4. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-009-03 (continued)	Stoker <sup>i</sup> (continued)	Multiple Cyclone/ Wet Scrubber <sup>c</sup> (continued)	Phenanthrene	3.10E-05 (1.33E-05)	---	D	FIRE <sup>q</sup>
			Pyrene	7.10E-06 (3.05E-06)	---	D	FIRE <sup>q</sup>

<sup>a</sup>Emission factors are in lb (g) of pollutant per MMBtu (MJ) of heat input.

<sup>b</sup>Source operated at 40,300 to 56,000 lb (18,280 to 25,400 kg) steam/hr firing pine/fir hog fuel and chips.

<sup>c</sup>Multiple cyclones without flyash reinjection.

<sup>d</sup>Data suspect; no emission factor developed.

<sup>e</sup>Source operated at 40,750 to 46,000 (18,484 to 20,865 kg) lb steam/hr firing sander dust fuel.

<sup>f</sup>Sources operated at 165,820 to 174,400 lb (75,215 to 79,107 kg) steam/hr firing pine/fir hog fuel and chips.

<sup>g</sup>Source operated at 91,500 to 93,000 lb (41,504 to 42,184 kg) steam/hr firing pine/fir chips.

<sup>h</sup>Source operated at 90,000 lb (40,824 kg) steam/hr firing pine/cedar hog fuel.

<sup>i</sup>Source operated at 117,000 to 126,000 lb (53,071 to 57,153 kg) steam/hr firing redwood/fir hog fuel.

<sup>j</sup>Source Emission Testing of the CE Wood-Fired Boiler at Rosenburg Forest Products (TAC Site #3). Performed for the Timber Association of California. Galston Technical Services, January 1991.

<sup>k</sup>Source Emission Testing of the Wood-fired Boiler at Big Valley Timber Company, Bieber, California. Performed for the Timber Association of California. Galston Technical Services, February, 1991.

<sup>l</sup>Source Emission Testing of the Wood-fired Boiler Exhaust at Bohemia, Inc., Rocklin, California. Prepared for the Timber Association of California. Galston Technical Services, December 1990.

<sup>m</sup>Source Emission Testing of the Wood-Fired Boiler Exhaust at Sierra Pacific, Burney, California. Performed for the Timber Association of California. Galston Technical Services, February 1991.

<sup>n</sup>Source Emission Testing of the Wood-fired Boiler #1 Exhaust Stack at Wheelabrator Shasta Energy Company (TAC Site 9), Anderson, California. Performed for the Timber Association of California. Galston Technical Services, January 1991.

<sup>o</sup>Source Emission Testing of the Wood-fired Boiler at Yorke Energy, North Fork, California. Performed for the Timber Association of California. Galston Technical Services, January 1991.

<sup>p</sup>Source Emission Testing of the Wood-fired boiler at Catalyst Hudson, Inc., Anderson California. Performed for the Timber Association of California. Galston Technical Services, February 1991.

<sup>q</sup>Source Emission Testing of the Wood-fired Boiler #3 Exhaust at Georgia Pacific, Fort Bragg, California. Performed for the Timber Association of California. Galston Technical Services, February 1991.

TABLE 4.1.2-5. PAH EMISSION FACTORS FOR WOOD WASTE-FIRED INDUSTRIAL BOILERS <50,000 LB STEAM/HR

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-009-06	Fuel Cell <sup>b</sup>	Cyclone	Anthracene	<1.30E-07 (<5.59E-08)	D	FIRE <sup>d</sup>
			Fluoranthene	5.90E-07 (2.54E-07)	D	FIRE <sup>d</sup>
			Fluorene	<1.00E-06 (<4.30E-07)	D	FIRE <sup>d</sup>
			Naphthalene	4.90E-04 (2.11E-04)	D	FIRE <sup>d</sup>
			Phenanthrene	3.00E-06 (1.29E-06)	D	FIRE <sup>d</sup>
			Pyrene	3.10E-07 (1.33E-07)	D	FIRE <sup>d</sup>
1-02-009-06	Wood Waste Fired Boiler <sup>c</sup>	Wet Scrubber	Benz(a)anthracene	4.40E-07 (1.89E-07)	D	FIRE <sup>e</sup>
			Benzo(a)pyrene	3.42E-07 (1.47E-07)	D	FIRE <sup>e</sup>
			Benzo(b)fluoranthene	1.31E-07 (5.63E-08)	D	FIRE <sup>e</sup>
			Benzo(k)fluoranthene	6.83E-07 (2.94E-07)	D	FIRE <sup>e</sup>
			Chrysene	1.95E-07 (8.38E-08)	D	FIRE <sup>e</sup>
			Dibenz(a,h)anthracene	<2.57E-08 (<1.10E-08)	D	FIRE <sup>e</sup>
			Indeno(1,2,3-cd)pyrene	4.07E-07 (1.75E-07)	D	FIRE <sup>e</sup>

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(continued)

TABLE 4.1.2-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-009-06 (continued)	Wood Waste Fired Boiler <sup>c</sup> (continued)	Wet Scrubber (continued)	Acenaphthene	6.71E-07 (2.88E-07)	D	FIRE <sup>e</sup>
			Acenaphthylene	3.72E-05 (1.60E-05)	D	FIRE <sup>e</sup>
			Anthracene	8.35E-06 (3.59E-06)	D	FIRE <sup>e</sup>
			Benzo(ghi)perylene	1.09E-06 (4.69E-07)	D	FIRE <sup>e</sup>
			Fluoranthene	9.52E-06 (4.09E-06)	D	FIRE <sup>e</sup>
			Fluorene	8.57E-06 (3.68E-06)	D	FIRE <sup>e</sup>
			Naphthalene	9.30E-05 (4.00E-05)	D	FIRE <sup>e</sup>
			Phenanthrene	6.18E-05 (2.66E-05)	D	FIRE <sup>e</sup>
			Pyrene	9.95E-06 (4.28E-06)	D	FIRE <sup>e</sup>

<sup>a</sup>Emission factors are in lb (g) of pollutants per MMBtu (MJ) of heat input.

<sup>b</sup>Source operated at 6,400 to 6,802 lb (2,903 to 3,085 kg) steam/hr firing fir sawdust fuel.

<sup>c</sup>Boiler of unknown design operated at 13,000 to 34,000 (5,897 to 15,422 kg) steam/hr firing cedar chips.

<sup>d</sup>Source Emission Testing of the Wood-fired Boiler Exhaust at Miller Redwood Co., Crescent City, California. Performed for the Timber Association of California. Galston Technical Services, February 1991.

<sup>e</sup>Determination of AB 2588 Emissions from a Wood-fired Boiler Exhaust, February 10 - 13, 1992. (Confidential Report No. ERC-63).

TABLE 4.1.2-6. PAH EMISSION FACTORS FOR NATURAL GAS-FIRED UTILITY BOILERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-01-006-01	Opposed Fired Boiler <sup>b</sup>	None	Fluorene	2.0E-09 (8.6E-10)	D	Booth et al., 1992
			Naphthalene	4.5E-08 (1.9E-08)	D	Booth et al., 1992
			Phenanthrene	3.7E-09 (1.6E-09)	D	Booth et al., 1992
1-01-006-01	Opposed Fired Boiler <sup>c</sup>	Flue Gas Recirculation	Chrysene	1.45E-08 (6.3E-09)	D	FIRE <sup>d</sup>
			Acenaphthene	4.57E-05 (2.0E-05)	D	FIRE <sup>d</sup>
			Acenaphthylene	1.85E-08 (8.0E-09)	D	FIRE <sup>d</sup>
			Anthracene	1.25E-08 (5.4E-09)	D	FIRE <sup>d</sup>
			Fluoranthene	5.02E-08 (2.2E-08)	D	FIRE <sup>d</sup>
			Fluorene	1.45E-07 (6.2E-08)	D	FIRE <sup>d</sup>
			Naphthalene	4.78E-05 (2.1E-05)	D	FIRE <sup>d</sup>
			Phenanthrene	1.80E-07 (7.7E-08)	D	FIRE <sup>d</sup>
			Pyrene	4.75E-08 (2.0E-08)	D	FIRE <sup>d</sup>

<sup>a</sup>Emission factors are in lb (g) per MMBtu (MJ) of heat input.

<sup>b</sup>2,561 MMBtu/hr (750 MW) opposed fired utility boiler firing natural gas.

<sup>c</sup>785 MMBtu/hr (230 MW) opposed fired utility boiler operating at 372 to 758 MMBtu/hr (109 to 222 MW) firing natural gas.

<sup>d</sup>Air Toxics “Hot Spots” Source Testing of a Utility Boiler, May 1991. (Confidential Report No. ERC-17).



TABLE 4.1.2-7. PAH EMISSION FACTORS FOR NATURAL GAS-FIRED INDUSTRIAL AND COMMERCIAL/INSTITUTIONAL BOILERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMCF (g/kL) <sup>a</sup>	Emission Factor Range in lb/MMCF (g/kL) <sup>a</sup>	Emission Factor Rating	Reference
1-02-006-01, -02, -03	b	None	Fluoranthene	8.69E-07 (1.39E-05)	ND - 8.69E-6 (ND - 1.39E-4)	D	Suprenant et al., 1981
			Naphthalene	4.24E-06 (6.80E-05)	ND - 1.47E-5 (ND - 2.35E-4)	D	Suprenant et al., 1981
			Phenanthrene	2.52E-07 (4.04E-06)	ND - 1.68E-6 (ND - 2.69E-5)	D	Suprenant et al., 1981
			Pyrene	1.97E-07 (3.16E-06)	ND - 1.12E-6 (ND - 1.79E-5)	D	Suprenant et al., 1981
			2-Methyl phenanthrene	1.37E-08 (2.19E-07)	ND - 1.37E-7 (ND - 2.19E-6)	D	Suprenant et al., 1981
			Carbazole	7.74E-08 (1.24E-06)	ND - 7.74E-7 (ND - 1.24E-5)	D	Suprenant et al., 1981
1-03-006-01 1-03-006-02	c	None	Acenaphthylene	4.99E-06 (8.0E-05)	ND - 2.04E-5 (ND - 3.26E-4)	D	Johnson et al., 1990
			Fluoranthene	4.37E-07 (7.0E-06)	ND - 2.12E-6 (ND - 3.40E-5)	D	Johnson et al., 1990
			Naphthalene	1.75E-05 (2.8E-04)	ND - 8.62E-5 (ND - 1.38E-3)	D	Suprenant et al., 1981
			Phenanthrene	6.24E-07 (1.0E-05)	ND - 3.37E-6 (ND - 5.40E-5)	D	Johnson et al., 1990
			Pyrene	1.87E-06 (3.0E-05)	ND - 8.18E-6 (ND - 1.31E-4)	D	Johnson et al., 1990

ND: Not Detected.

<sup>a</sup>Emission factors are in lb (g) per MMCF (kL) of natural gas fired.

<sup>b</sup>Average emission factors based on 10 units tested: 2 firetube, 1 scotch, 7 watertube. Rated capacity range: 7.2 to 178 MMBtu/hr (2.4 to 52MW).

<sup>c</sup>Average emission factors based on 5 packaged watertube boilers tested. Rated capacity range: 17.4 to 126 MMBtu/hr (5.1 to 37 MW).

TABLE 4.1.2-8. PAH EMISSION FACTORS FOR ANTHRACITE COAL COMBUSTION

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-001-02, 1-02-001-04	Stoker	None	Naphthalene	0.13 (0.065)	E	U.S. EPA, 1995b
			Phenanthrene	6.8E-03 (3.4E-03)	E	U.S. EPA, 1995b

<sup>a</sup>Emission factors are in lb (kg) per ton (Mg) of coal fired.

TABLE 4.1.2-9. PAH EMISSION FACTORS FOR COAL-FIRED UTILITY BOILERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-002-01	Pulverized Bituminous Wet-Bottom <sup>b</sup>	c	Benzo(a)pyrene	1.94E-04 (9.72E-05) <sup>d</sup>	ND - 1.17E-03 (ND - 5.83E-04)	E	Johnson et al., 1990
			Benzo(b)fluoranthene	6.94E-05 (3.47E-05)	ND - 4.16E-04 (ND - 2.08E-04)	D	Johnson et al., 1990
			Chrysene	2.16E-04 (1.08E-04)	ND - 1.29E-03 (ND - 6.47E-04)	D	Johnson et al., 1990
			Indeno(1,2,3-cd)pyrene	6.22E-05 (3.11E-05)	ND - 3.74E-04 (ND - 1.87E-04)	D	Johnson et al., 1990
			Benzo(ghi)perylene	4.16E-05 (2.08E-05)	ND - 2.50E-04 (ND - 1.25E-04)	D	Johnson et al., 1990
			Fluoranthene	1.70E-04 (8.48E-05)	ND - 1.02E-03 (ND - 5.10E-04)	D	Johnson et al., 1990
			Naphthalene	1.46E-04 (7.29E-05)	ND - 4.37E-04 (ND - 2.18E-04)	D	Shih et al., 1980
			Phenanthrene	5.34E-04 (2.67E-04)	ND - 3.08E-03 (ND - 1.54E-03)	D	Johnson et al., 1990
			Pyrene	3.76E-04 (1.88E-04)	ND - 2.26E-03 (ND - 1.13E-03)	D	Johnson et al., 1990
1-01-002-02	Pulverized Bituminous Dry-Bottom <sup>e</sup>	f	Benz(a)anthracene	1.68E-06 (8.40E-07)	ND - 6.04E-06 (ND - 3.02E-06)	D	Johnson et al., 1990
			Benzo(a)pyrene	1.32E-05 (6.58E-06)	ND - 9.60E-05 (ND - 4.80E-05)	D	Johnson et al., 1990
			Benzo(b)fluoranthene	1.46E-06 (7.30E-07)	ND - 3.46E-06 (ND - 1.73E-06)	D	Johnson et al., 1990

TABLE 4.1.2-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-002-02 (continued)	Pulverized Bituminous Dry-Bottom <sup>e</sup> (continued)	f	Benzo(k)fluoranthene	8.60E-07 (4.30E-07)	ND - 3.10E-06 (ND - 1.55E-06)	D	Johnson et al., 1990
			Chrysene	2.96E-06 (1.48E-06)	ND - 1.11E-05 (ND - 5.54E-06)	D	Johnson et al., 1990
			Dibenz(a,h)anthracene	4.60E-06 (2.30E-06)	ND - 1.25E-05 (ND - 6.27E-06)	D	Johnson et al., 1990
			Indeno(1,2,3-cd)pyrene	2.40E-07 (1.20E-07)	ND - 2.40E-06 (ND - 1.20E-06)	D	Johnson et al., 1990
			Acenaphthene	5.80E-07 (2.90E-07)	ND - 1.46E-06 (ND - 7.30E-07)	D	Johnson et al., 1990
			Acenaphthylene	1.02E-06 (5.10E-07)	ND - 3.24E-06 (ND - 1.62E-06)	D	Johnson et al., 1990
			Anthracene	1.70E-06 (8.50E-07)	ND - 4.44E-06 (ND - 2.22E-06)	D	Johnson et al., 1990
			Benzo(ghi)perylene	9.76E-06 (4.88E-06)	ND - 2.76E-05 (ND - 1.38E-05)	D	Johnson et al., 1990
			Fluoranthene	9.00E-06 (4.50E-06)	ND - 3.10E-05 (ND - 1.55E-05)	D	Johnson et al., 1990
			Fluorene	1.38E-06 (6.90E-07)	ND - 5.36E-06 (ND - 2.68E-06)	D	Johnson et al., 1990
			Naphthalene	6.89E-04 (3.45E-04)	ND - 3.77E-03 (ND - 1.89E-03)	D	Shih et al., 1980
			Phenanthrene	1.88E-05 (9.38E-06)	ND - 6.28E-05 (ND - 3.14E-05)	D	Johnson et al., 1990

(continued)

TABLE 4.1.2-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-002-02 (continued)	Pulverized Bituminous Dry-Bottoms (continued)	f	Pyrene	9.46E-06 (4.73E-06)	ND - 3.40E-05 (ND - 1.70E-05)	D	Johnson et al., 1990
			1-Nitropyrene	2.48E-06 (1.24E-06)	4.80E-07 - 4.60E-06 (2.40E-07 - 2.30E-06)	D	Johnson et al., 1990
			Benzo(a)fluorene	4.86E-06 (2.43E-06)	1.46E-06 - 7.80E-06 (7.30E-07 - 3.90E-06)	D	Johnson et al., 1990
			Benzo(e)pyrene	2.60E-07 (1.30E-07)	ND - 4.80E-07 (ND - 2.40E-07)	D	Johnson et al., 1990
			Methylanthracenes	1.01E-05 (5.04E-06)	2.00E-06 - 3.30E-05 (1.00E-06 - 1.65E-05)	D	Johnson et al., 1990
			Methylphenanthrenes	2.92E-06 (1.46E-06)	ND - 1.42E-05 (N - 7.10E-06)	D	Johnson et al., 1990
			Triphenylene	1.00E-07 (5.00E-08)	ND - 2.20E-05 (ND - 1.10E-05)	D	Johnson et al., 1990
1-01-002-03	Bituminous Cyclone <sup>g</sup>	ESP	Benz(a)anthracene	3.72E-09 (1.60E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(a)pyrene	1.16E-09 (5.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(b+k)fluoranthene	6.98E-09 (3.00E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Chrysene	8.84E-09 (3.80E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Dibenz(a,h)anthracene	1.16E-09 (5.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994

(continued)

TABLE 4.1.2-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-002-03 (continued)	Bituminous Cyclone <sup>g</sup> (continued)	ESP (continued)	Indeno(1,2,3-cd)pyrene	6.98E-10 (3.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Acenaphthene	2.65E-08 (1.14E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Acenaphthylene	6.75E-09 (2.90E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Anthracene	2.07E-08 (8.90E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(ghi)perylene	1.16E-09 (5.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Fluoranthene	2.70E-08 (1.16E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Fluorene	3.14E-08 (1.35E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Naphthalene	2.15E-07 (9.26E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Phenanthrene	7.77E-08 (3.34E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Pyrene	1.40E-08 (6.00E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			1-Methylnaphthalene	1.58E-08 (6.80E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			2-Methylnaphthalene	3.74E-08 (1.61E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994

(continued)

TABLE 4.1.2-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-002-03 (continued)	Bituminous Cyclone <sup>g</sup> (continued)	ESP (continued)	Benzo(e)pyrene	2.09E-09 (9.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
1-01-002-03	Bituminous Cyclone <sup>i</sup>	Baghouse/ SNOX <sup>j</sup>	Benzo(a)anthracene	2.09E-09 (9.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(a)pyrene	9.30E-10 (4.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(b+k)fluoranthene	3.95E-09 (1.70E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Chrysene	2.09E-09 (9.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Dibenz(a,h)anthracene	6.98E-10 (3.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Indeno(1,2,3-cd)pyrene	9.30E-10 (4.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Acenaphthene	5.35E-09 (2.30E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Acenaphthylene	4.19E-09 (1.80E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Anthracene	3.49E-09 (1.50E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(ghi)perylene	9.30E-10 (4.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Fluoranthene	6.98E-09 (3.00E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994

(continued)

TABLE 4.1.2-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-002-03 (continued)	Bituminous Cyclone <sup>i</sup> (continued)	Baghouse/ SNOX <sup>j</sup> (continued)	Fluorene	6.98E-10 (3.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Naphthalene	5.98E-08 (2.57E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Phenanthrene	2.42E-08 (1.04E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Pyrene	1.16E-09 (5.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			1-Methylnaphthalene	1.14E-08 (4.90E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			2-Methylnaphthalene	2.00E-08 (8.60E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(e)pyrene	1.16E-09 (5.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
1-01-003-01, 06	Lignite Utility Boiler <sup>k</sup>	1	Benz(a)anthracene	1.40E-07 (7.00E-08)	ND - 5.80E-07 (ND - 2.90E-07)	D	Johnson et al., 1990
			Benzo(a)pyrene	6.60E-07 (3.30E-07)	ND - 1.90E-06 (ND - 9.50E-07)	D	Johnson et al., 1990
			Benzo(b)fluoranthene	4.00E-07 (2.00E-07)	ND - 1.86E-06 (ND - 9.30E-07)	D	Johnson et al., 1990
			Benzo(k)fluoranthene	3.00E-07 (1.50E-07)	ND - 1.38E-06 (ND - 6.90E-07)	D	Johnson et al., 1990
			Chrysene	2.40E-07 (1.20E-07)	ND - 1.08E-06 (ND - 5.40E-07)	D	Johnson et al., 1990

(continued)



TABLE 4.1.2-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-003-01, 06 (continued)	Lignite Utility Boiler <sup>k</sup> (continued)	1	Indeno(1,2,3-cd)pyrene	6.40E-07 (3.20E-07)	ND - 1.18E-06 (ND - 5.90E-07)	D	Johnson et al., 1990
			Anthracene	3.40E-07 (1.70E-07)	ND - 1.08E-06 (ND - 5.40E-07)	D	Johnson et al., 1990
			Benzo(ghi)perylene	1.78E-06 (8.90E-07)	ND - 7.80E-06 (ND - 3.90E-06)	D	Johnson et al., 1990
			Fluoranthene	2.80E-07 (1.40E-07)	ND - 1.32E-06 (ND - 6.60E-07)	D	Johnson et al., 1990
			Fluorene	1.40E-07 (7.00E-08)	ND - 3.60E-07 (ND - 1.80E-07)	D	Johnson et al., 1990
			Phenanthrene	4.40E-07 (2.20E-07)	ND - 1.86E-06 (ND - 9.30E-07)	D	Johnson et al., 1990
			Pyrene	2.80E-06 (1.40E-06)	ND - 1.38E-05 (ND - 6.90E-06)	D	Johnson et al., 1990
			1-Nitropyrene	3.20E-06 (1.60E-06)	8.40E-07 - 5.60E-06 (4.20E-07 - 2.80E-06)	D	Johnson et al., 1990
			Benzo(a)fluorene	3.00E-07 (1.50E-07)	ND - 4.80E-07 (ND - 2.40E-07)	D	Johnson et al., 1990
			Benzo(e)pyrene	1.46E-06 (7.30E-07)	ND - 8.00E-06 (ND - 4.00E-06)	D	Johnson et al., 1990
			Dibenz(a,h)acridine	4.00E-07 (2.00E-07)	ND - 7.20E-07 (ND - 3.60E-07)	D	Johnson et al., 1990
			Methylanthracenes	1.70E-06 (8.50E-07)	1.20E-06 - 1.86E-06 (6.00E-07 - 9.30E-07)	D	Johnson et al., 1990

(continued)

TABLE 4.1.2-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-003-01, 06 (continued)	Lignite Utility Boiler <sup>k</sup> (continued)	1	Triphenylene	4.00E-08 (2.00E-08)	ND - 1.00E-07 (ND - 5.00E-08)	D	Johnson et al., 1990
1-01-003-02	Pulverized Lignite Tangential Dry Bottom <sup>m</sup>	ESP/Wet FGD <sup>n</sup>	Benz(a)anthracene	2.09E-09 (9.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(a)pyrene	9.30E-10 (4.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(b+k)fluoranthene	4.42E-09 (1.90E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Chrysene	5.35E-09 (2.30E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Dibenz(a,h)anthracene	6.98E-10 (3.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Indeno(1,2,3-cd)pyrene	6.98E-10 (3.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Acenaphthene	1.72E-08 (7.40E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Acenaphthylene	1.05E-08 (4.50E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Anthracene	1.47E-08 (6.30E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(ghi)perylene	6.98E-10 (3.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Fluoranthene	4.23E-08 (1.82E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994

(continued)

TABLE 4.1.2-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-01-003-02 (continued)	Pulverized Lignite Tangential Dry Bottom <sup>m</sup> (continued)	ESP/Wet FGD <sup>n</sup> (continued)	Fluorene	4.16E-08 (1.79E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Naphthalene	2.56E-07 (1.10E-07) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Phenanthrene	3.14E-07 (1.35E-07) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Pyrene	1.63E-08 (7.00E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			1-Methylnaphthalene	1.51E-08 (6.50E-09) <sup>h</sup>	---	D	Sverdrup et al., 1994
			2-Methylnaphthalene	4.09E-08 (1.76E-08) <sup>h</sup>	---	D	Sverdrup et al., 1994
			Benzo(e)pyrene	1.16E-09 (5.00E-10) <sup>h</sup>	---	D	Sverdrup et al., 1994

ND: Not Detected.

<sup>a</sup>Emission factors are in lb (kg) per ton (Mg) of coal fired, unless otherwise noted.

<sup>b</sup>Composite average emission factors based on six tested bituminous pulverized coal fired wet-bottom utility boilers. Rated capacity range: 376 to 2,834 MMBtu/hr (110 to 830 MW).

<sup>c</sup>Four of six tested units ESP controlled, one mechanical precipitator/ESP controlled and one wet scrubber controlled.

<sup>d</sup>Laboratory analysis was unable to resolve benzo(a)pyrene and benzo(e)pyrene.

<sup>e</sup>Composite average emission factors based on six pulverized bituminous coal fired dry-bottom utility boilers. Rated capacity range: 263 to 1,707 MMBtu/hr (77 to 500 MW).

<sup>f</sup>Three of six tested units ESP controlled, two multicyclone/ESP controlled and one wet scrubber controlled.

<sup>g</sup>Bituminous coal fired cyclone utility boiler with four cyclone burners. Rated capacity: 369 MMBtu/hr (108 MW).

(continued)

TABLE 4.1.2-9. (Continued)

<sup>h</sup>Emission factors are in lb (g) per MMBtu (MJ) of heat input.

<sup>i</sup>Bituminous coal fired cyclone utility boiler with four cyclone burners. Rated capacity: 369 MMBtu/hr (108 MW).

<sup>j</sup>Testing was conducted during an SNOX demonstration program. The SNOX process combines selective catalytic reduction (SCR) with wet sulfuric acid technologies to remove nitrogen and sulfur oxides from the flue gas. A slip stream (35 MW) was taken after the air preheater and before the ESP for the demonstration.

<sup>k</sup>Composite average emission factors based on nine lignite coal fired utility boilers, Five pulverized dry-bottom, two cyclone and two spreader stokers. Rated capacity range:

68 to 1,434 MMBtu/hr (20 to 420 MW).

<sup>l</sup>Nine tested units multicyclone or ESP controlled.

<sup>m</sup>Pulverized lignite coal fired tangential dry-bottom utility boiler. Rated capacity: 3,756 MMBtu/hr (1,100 MW).

<sup>n</sup>ESP followed by a flue gas desulfurization (FGD) system consisting of four countercurrent spray towers using an alkali slurry.

TABLE 4.1.2-10. PAH EMISSION FACTORS FOR COAL-FIRED INDUSTRIAL AND COMMERCIAL/INSTITUTIONAL BOILERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-02-002-01, 1-02-002-02	Pulverized Bituminous Wet and Dry-Bottom <sup>b</sup>	<sup>c</sup>	Benzo(a)pyrene	2.80E-07 (1.40E-07)	ND - 1.90E-06 (ND - 9.50E-07)	D	Johnson et al., 1990
			Dibenz(a,h)anthracene	2.40E-05 (1.20E-05)	---	D	Johnson et al., 1990
			Indeno(1,2,3-cd)pyrene	5.60E-06 (2.80E-06)	---	D	Johnson et al., 1990
			Anthracene	3.60E-06 (1.80E-06)	ND - 2.20E-05 (ND - 1.10E-05)	D	Johnson et al., 1990
			Benzo(ghi)perylene	8.00E-08 (4.00E-08)	ND - 4.48E-07 (ND - 2.24E-07)	D	Johnson et al., 1990
			Fluoranthene	4.80E-05 (2.40E-05)	ND - 3.00E-04 (ND - 1.50E-04)	D	Johnson et al., 1990
			Phenanthrene	1.68E-05 (8.40E-06)	ND - 1.01E-04 (ND - 5.04E-05)	D	Johnson et al., 1990
			Pyrene	3.80E-06 (1.90E-06)	ND - 1.24E-05 (ND - 6.20E-06)	D	Johnson et al., 1990
			Benzo(e)pyrene	7.80E-07 (3.90E-07)	ND - 5.40E-06 (ND - 2.70E-06)	D	Johnson et al., 1990
			Benzofluoranthenes	6.20E-04 (3.10E-04)	---	D	Johnson et al., 1990

TABLE 4.1.2-10. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-02-002-04	Bituminous Stoker <sup>d</sup>	<sup>e</sup>	Benz(a)anthracene	8.40E-07 (4.20E-07)	---	D	Johnson et al., 1990
			Benzo(a)pyrene	4.60E-05 (2.30E-05)	3.40E-07 - 6.20E-04 (1.70E-07 - 3.10E-04)	D	Johnson et al., 1990
			Chrysene	2.20E-06 (1.10E-06)	4.40E-07 - 4.60E-06 (2.20E-07 - 2.30E-06)	D	Johnson et al., 1990
			Indeno(1,2,3-cd)pyrene	1.24E-06 (6.20E-07)	ND - 5.00E-06 (ND - 2.50E-06)	D	Johnson et al., 1990
			Acenaphthene	1.94E-04 (9.71E-05)	---	D	Johnson et al., 1990
			Acenaphthylene	3.68E-05 (1.84E-05)	---	D	Johnson et al., 1990
			Anthracene	4.84E-05 (2.42E-05)	---	D	Johnson et al., 1990
			Benzo(ghi)perylene	2.20E-05 (1.10E-05)	ND - 2.80E-04 (ND - 1.40E-04)	D	Johnson et al., 1990
			Fluoranthene	2.52E-04 (1.26E-04)	ND - 2.40E-03 (ND - 1.20E-03)	D	Johnson et al., 1990
			Fluorene	4.00E-05 (2.00E-05)	ND - 1.60E-04 (ND - 8.00E-05)	D	Johnson et al., 1990
			Naphthalene	1.93E-03 (9.65E-04)	ND - 7.73E-03 (ND - 3.86E-03)	D	Suprenant et al., 1981
Phenanthrene	3.08E-04 (1.54E-04)	ND - 3.05E-03 (ND - 1.53E-03)	D	Johnson et al., 1990			

(continued)

TABLE 4.1.2-10. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-02-002-04 (continued)	Bituminous Stoker <sup>d</sup> (continued)	<sup>e</sup>	Pyrene	2.36E-04 (1.18E-04)	ND - 2.90E-03 (ND - 1.45E-03)	D	Johnson et al., 1990
			Benzo(a)fluorene	1.90E-06 (9.50E-07)	ND - 7.60E-06 (ND - 3.80E-06)	D	Johnson et al., 1990
			Benzo(e)pyrene	3.80E-05 (1.90E-05)	3.40E-07 - 4.80E-04 (1.70E-07 - 2.40E-04)	D	Johnson et al., 1990
			Benzo(a)fluoranthene	1.46E-06 (7.30E-07)	4.40E-07 - 5.00E-06 (2.20E-07 - 2.50E-06)	D	Johnson et al., 1990
			Coronene	2.20E-06 (1.10E-06)	ND - 2.00E-05 (ND - 1.00E-05)	D	Johnson et al., 1990
			Perylene	6.20E-06 (3.10E-06)	ND - 9.80E-05 (ND - 4.90E-05)	D	Johnson et al., 1990
1-03-002-08	Bituminous Stoker <sup>f</sup>	None	Benz(a)anthracene	7.39E-03 (3.70E-03)	---	E	Johnson et al., 1990
			Benzo(a)pyrene	9.97E-03 (4.98E-03)	---	E	Johnson et al., 1990
			Chrysene	1.23E-03 (6.16E-04)	---	E	Johnson et al., 1990
			Dibenz(a,h)anthracene	1.40E-03 (7.00E-04)	---	E	Johnson et al., 1990
			Benzo(ghi)perylene	2.69E-03 (1.34E-03)	---	E	Johnson et al., 1990
			Fluoranthene	1.38E-02 (6.92E-03)	---	E	Johnson et al., 1990

(continued)

TABLE 4.1.2-10. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
1-03-002-08 (continued)	Bituminous Stoker <sup>f</sup> (continued)	None	Naphthalene	1.05E-02 (5.24E-03)	---	E	Suprenant et al., 1981
			Phenanthrene	1.62E-02 (8.09E-03)	---	E	Johnson et al., 1990
			Pyrene	1.39E-02 (6.97E-03)	---	E	Johnson et al., 1990
			Methylphenanthrenes	2.13E-03 (1.06E-03)	---	E	Johnson et al., 1990

<sup>a</sup>Emission factors are in lb (kg) per ton (Mg) of coal fired.

<sup>b</sup>Composite average emission factors based on seven pulverized bituminous coal fired wet and dry-bottom industrial boilers. Rated capacity range: 116 to 1,251 MMBtu/hr (34 to 366 MW).

<sup>c</sup>Three of seven tested units ESP controlled, five multicyclone controlled and one FGD unit.

<sup>d</sup>Composite average emission factors based on 11 bituminous coal fired spreader stokers, five overfeed stokers and one underfeed stoker.

<sup>e</sup>Eleven units tested. Control configurations included multicyclone, ESP and uncontrolled.

<sup>f</sup>Bituminous coal fired underfeed stoker. Rated Capacity: 2.2 MMBtu/hr (0.63 MW).



TABLE 4.1.2-11. PAH EMISSION FACTORS FOR OIL-FIRED BOILERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-01-004-01	Residual Oil-Fired Utility Boiler <sup>b</sup>	None	Benz(a)anthracene	<sup>c</sup>	6.40E-10 - 1.02E-07 (2.75E-10 - 4.39E-08)	NA	Booth, 1992
			Benzo(a)pyrene	<sup>c</sup>	6.32E-09 - 9.22E-09 (2.72E-09 - 3.96E-09)	NA	Booth, 1992
			Benzo(b)fluoranthene	<sup>c</sup>	6.40E-09 - 3.65E-08 (2.75E-09 - 1.57E-08)	NA	Booth, 1992
			Benzo(k)fluoranthene	<sup>c</sup>	6.40E-09 - 3.65E-08 (2.75E-09 - 1.57E-08)	NA	Booth, 1992
			Chrysene	<sup>c</sup>	6.40E-09 - 1.75E-08 (2.75E-09 - 7.52E-09)	NA	Booth, 1992
			Dibenz(a,h)anthracene	<sup>c</sup>	6.40E-09 - 2.47E-08 (2.75E-09 - 1.06E-08)	NA	Booth, 1992
			Indeno(1,2,3-cd)pyrene	<sup>c</sup>	6.40E-09 - 6.25E-08 (2.75E-09 - 2.69E-08)	NA	Booth, 1992
			Acenaphthene	<sup>c</sup>	6.32E-09 - 1.02E-07 (2.72E-09 - 4.39E-08)	NA	Booth, 1992
			Acenaphthylene	<sup>c</sup>	6.32E-09 - 9.22E-09 (2.72E-09 - 3.96E-09)	NA	Booth, 1992
			Anthracene	<sup>c</sup>	6.32E-09 - 1.43E-08 (2.72E-09 - 6.15E-09)	NA	Booth, 1992
			Benz(ghi)perylene	<sup>c</sup>	6.40E-09 - 6.95E-08 (2.75E-09 - 2.99E-08)	NA	Booth, 1992
			Fluoranthene	<sup>c</sup>	6.40E-09 - 2.55E-08 (2.75E-09 - 1.10E-08)	NA	Booth, 1992

TABLE 4.1.2-11. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-01-004-01 (continued)	Residual Oil-Fired Utility Boiler <sup>b</sup> (continued)	None	Fluorene	<sup>c</sup>	6.40E-09 - 3.15E-08 (2.75E-09 - 1.35E-08)	NA	Booth, 1992
			Naphthalene	<sup>c</sup>	4.23E-07 - 1.21E-05 (1.82E-07 - 5.20E-06)	NA	Booth, 1992
			Phenanthrene	<sup>c</sup>	6.40E-09 - 1.08E-07 (2.75E-09 - 4.64E-08)	NA	Booth, 1992
			Pyrene	<sup>c</sup>	6.40E-09 - 3.17E-08 (2.75E-09 - 1.36E-08)	NA	Booth, 1992
1-01-004-01	No. 6 Oil Wall-Fired Utility Boiler <sup>d</sup>	None	Benz(a)anthracene	<1.02E-07 (<4.39E-08)	---	D	FIRE <sup>g</sup>
			Chrysene	<4.55E-08 (<1.96E-08)	---	D	FIRE <sup>g</sup>
			Dibenz(a,h)anthracene	<2.47E-08 (<1.06E-08)	---	D	FIRE <sup>g</sup>
			Indeno(1,2,3-cd)pyrene	<6.25E-08 (<2.69E-08)	---	D	FIRE <sup>g</sup>
			Acenaphthene	<2.12E-08 (<9.11E-09)	---	D	FIRE <sup>g</sup>
			Anthracene	<1.43E-08 (<6.15E-09)	---	D	FIRE <sup>g</sup>
			Benz(ghi)perylene	<6.95E-08 (<2.99E-08)	---	D	FIRE <sup>g</sup>

TABLE 4.1.2-11. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-01-004-01 (continued)	No. 6 Oil Wall-Fired Utility Boiler <sup>d</sup> (continued)	None	Fluoranthene	<7.78E-08 (<3.34E-08)	---	D	FIRE <sup>g</sup>
			Fluorene	<1.12E-08 (<4.82E-09)	---	D	FIRE <sup>g</sup>
			Naphthalene	8.44E-06 (3.63E-06)	---	D	FIRE <sup>g</sup>
			Phenanthrene	<1.08E-07 (<4.64E-08)	---	D	FIRE <sup>g</sup>
			Pyrene	<7.07E-08 (<3.04E-08)	---	D	FIRE <sup>g</sup>
1-01-004-01	No. 6 Oil Wall-Fired Utility Boiler <sup>e</sup>	Flue Gas Recirculation	Acenaphthene	4.55E-07 (1.96E-07)	---	D	FIRE <sup>h</sup>
			Anthracene	<8.73E-09 (<3.75E-09)	---	D	FIRE <sup>h</sup>
			Fluoranthene	<9.41E-09 (<4.05E-09)	---	D	FIRE <sup>h</sup>
			Fluorene	2.55E-08 (1.10E-08)	---	D	FIRE <sup>h</sup>
			Naphthalene	2.67E-06 (1.15E-06)	---	D	FIRE <sup>h</sup>
			Phenanthrene	2.45E-08 (1.05E-08)	---	D	FIRE <sup>h</sup>

TABLE 4.1.2-11. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-01-004-01 (continued)	No. 6 Oil Wall-Fired Utility Boiler <sup>e</sup> (continued)	Flue Gas Recirculation (continued)	Pyrene	<8.42E-09 (<3.62E-09)	---	D	FIRE <sup>h</sup>
1-01-004-05	No. 5 Oil-Fired Utility Boiler <sup>f</sup>	Flue Gas Recirculation	Chrysene	1.45E-08 (6.23E-09)	---	D	FIRE <sup>i</sup>
			Acenaphthene	4.57E-05 (1.96E-05)	---	D	FIRE <sup>i</sup>
			Acenaphthylene	1.85E-08 (7.97E-09)	---	D	FIRE <sup>i</sup>
			Anthracene	1.25E-08 (5.37E-09)	---	D	FIRE <sup>i</sup>
			Fluoranthene	5.02E-08 (2.16E-08)	---	D	FIRE <sup>i</sup>
			Fluorene	1.45E-07 (6.25E-08)	---	D	FIRE <sup>i</sup>
			Naphthalene	4.78E-05 (2.06E-05)	---	D	FIRE <sup>i</sup>
			Phenanthrene	1.80E-07 (7.74E-08)	---	D	FIRE <sup>i</sup>
			Pyrene	4.75E-08 (2.04E-08)	---	D	FIRE <sup>i</sup>

TABLE 4.1.2-11. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-004-01	No. 6 Oil-Fired Industrial Boiler	None	Chrysene	1.40E-07 (6.02E-08)	---	D	FIRE <sup>j</sup>
			Benzo(b)fluoranthene	<2.00E-08 (<8.60E-09)	---	D	FIRE <sup>j</sup>
			Acenaphthylene	<7.40E-07 (<3.18E-07)	---	D	FIRE <sup>j</sup>
			Fluoranthene	<1.90E-07 (<8.17E-08)	---	D	FIRE <sup>j</sup>
			Fluorene	3.50E-07 (1.50E-07)	---	D	FIRE <sup>j</sup>
			Naphthalene	2.12E-04 (9.11E-05)	---	D	FIRE <sup>j</sup>
			Phenanthrene	5.10E-07 (2.19E-07)	---	D	FIRE <sup>j</sup>
			Pyrene	2.60E-08 (1.12E-08)	---	D	FIRE <sup>j</sup>
			2-Methylnaphthalene	9.80E-07 (4.21E-07)	---	D	FIRE <sup>j</sup>
1-02-005-01, 1-03-005-01	No. 2 Oil-Fired Boiler	None	Benzo(a)pyrene	<5.96E-09 (<2.56E-09)	ND - 3.58E-08 (ND - 1.54E-08)	E	Johnson et al., 1990
Fluoranthene			<1.91E-08 (<8.20E-09)	ND - 9.54E-08 (ND - 4.10E-08)	E	Johnson et al., 1990	

TABLE 4.1.2-11. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
1-02-005-01, 1-03-005-01 (continued)	No. 2 Oil-Fired Boiler <sup>g</sup> (continued)	None	Naphthalene	<5.00E-05 (<2.15E-05)	ND - 1.50E-04 (ND - 6.45E-05)	E	Suprenant et al., 1980
			Pyrene	<1.79E-08 (<7.69E-09)	ND - 8.34E-08 (ND - 3.59E-08)	E	Johnson et al., 1990

NA - Not Applicable.

ND - Not Detected.

<sup>a</sup>Emission factors are in lb (g) per MMBtu (MJ) of heat input.

<sup>b</sup>Multiple units tested. Boiler design: front or opposed fired. Rated capacity range: 188 to 2,523 MMBtu/hr (55 to 739 MW).

<sup>c</sup>Data not available to calculate mean emission factor. Median emission factor may be used.

<sup>d</sup>598 MMBtu/hr (175 MW) wall-fired utility boiler operated at nominal full load during testing.

<sup>e</sup>1,639 MMBtu/hr (480 MW) wall-fired utility boiler operated at nominal full load during testing.

<sup>f</sup>785 MMBtu/hr (230 MW) utility boiler operated over a range of load conditions during testing.

<sup>g</sup>Bell, Arlene C., and Booth, Richard B. Emissions Inventory Testing at El Segundo Generating Station Unit 1. Prepared for Southern California Edison Company, Rosemead, California. For Inclusion in Air Toxics Hot Spots Inventory Required under AB-2588. CARNOT, Tustin, California. ESR 53304-2052. April 1990.

<sup>h</sup>McDannel, Mark D. and Green, Lisa A. Air Toxics Emissions Inventory Testing at Alamitos Unit 5. Prepared for Southern California Edison Company, Rosemead, California. For Inclusion in Air Toxics Hot Spots Inventory Required under AB-2588. CARNOT, Tustin, California. ESR 53304-2053. May 1990.

<sup>i</sup>Air Toxics "Hot Spots" Source Testing of a Utility Boiler, May 1991. (Confidential Report No. ERC-17).

<sup>j</sup>AB 2588 Testing of an Industrial Boiler at a Creamery, March 5 through 22, 1990. (Confidential Report No. ERC-65).

TABLE 4.1.2-12. PAH EMISSION FACTORS FOR OIL-FIRED PROCESS HEATERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
3-10-004-02	Residual Oil-Fired Pipeline Heater	None	Benz(a)anthracene	<5.51E-05 (<2.37E-05)	D	FIRE <sup>b</sup>
			Chrysene	<1.07E-05 (<4.60E-06)	D	FIRE <sup>b</sup>
			Dibenz(a,h)anthracene	7.72E-06 (3.32E-06)	D	FIRE <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	5.10E-06 (2.19E-06)	D	FIRE <sup>b</sup>
			Anthracene	<1.52E-05 (<6.54E-06)	D	FIRE <sup>b</sup>
			Benz(ghi)perylene	1.38E-05 (5.93E-06)	D	FIRE <sup>b</sup>
			Fluoranthene	3.21E-05 (1.38E-05)	D	FIRE <sup>b</sup>
			Fluorene	1.96E-04 (8.43E-05)	D	FIRE <sup>b</sup>
			Naphthalene	2.71E-04 (1.17E-04)	D	FIRE <sup>b</sup>
			Phenanthrene	3.38E-04 (1.45E-04)	D	FIRE <sup>b</sup>
Pyrene	9.46E-05 (4.07E-05)	D	FIRE <sup>b</sup>			

<sup>a</sup>Emission factors are in lb (g) per MMBtu (MJ) of heat input.

<sup>b</sup>Emissions Inventory Testing at Huntington Beach Generating Station Fuel Oil Heater No. 2. Prepared for Southern California Edison Company, Rosemead, California. CARNOT, May 1990.

TABLE 4.1.2-13. PAH EMISSION FACTORS FOR WASTE OIL COMBUSTION

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1000 gal (kg/1000 l) <sup>a</sup>	Emission Factor Rating	Reference
1-05-001-14, 1-05-002-14	Space Heater - Vaporizing Burner	None	Benz(a)anthracene/Chrysene	4.0E-03 (4.8E-04)	D	U.S. EPA, 1995c
			Benzo(a)pyrene	4.0E-03 (4.8E-04)	D	U.S. EPA, 1995c
			Benzofluoranthenes	4.02E-04 (4.83E-05)	D	Cooke et al., 1984
			Acenaphthylene	1.34E-04 (1.61E-05)	D	Cooke et al., 1984
			Anthracene/Phenanthrene	1.10E-02 (1.3E-03)	D	U.S. EPA, 1995c
			Fluorene	4.42E-04 (5.31E-05)	D	Cooke et al., 1984
			Naphthalene	1.30E-02 (1.6E-03)	D	U.S. EPA, 1995c
			Pyrene	7.1E-03 (8.4E-04)	D	U.S. EPA, 1995c
			Benzo(e)pyrene	7.37E-04 (8.85E-05)	D	Cooke et al., 1984
			Perylene	4.02E-04 (4.83E-05)	D	Cooke et al., 1984
1-05-001-13, 1-05-002-13	Space Heater - Atomizing Burner	None	Benz(a)anthracene	3.52E-05 (4.22E-06)	D	Cooke et al., 1984
			Benzo(a)pyrene	5.86E-05 (7.04E-06)	D	Cooke et al., 1984

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(continued)



TABLE 4.1.2-13. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1000 gal (kg/1000 l) <sup>a</sup>	Emission Factor Rating	Reference
1-05-001-13, 1-05-002-13 (continued)	Space Heater - Atomizing Burner (continued)	None	Chrysene	3.52E-05 (4.22E-06)	D	Cooke et al., 1984
			Indeno(1,2,3-cd)pyrene	4.69E-05 (5.63E-06)	D	Cooke et al., 1984
			Acenaphthene	2.93E-05 (3.52E-06)	D	Cooke et al., 1984
			Anthracene/Phenanthrene	1.0E-04 (1.2E-05)	D	U.S. EPA, 1995c
			Benzo(ghi)perylene	4.11E-05 (4.93E-06)	D	Cooke et al., 1984
			Fluoranthene	5.82E-05 (6.34E-06)	D	Cooke et al., 1984
			Fluorene	8.80E-05 (1.06E-05)	D	Cooke et al., 1984
			Naphthalene	9.2E-05 (1.1E-05)	D	U.S. EPA, 1995c
			Pyrene	8.3E-06 (9.95E-07)	D	U.S. EPA, 1995c
			Anthanthrene	1.17E-05 (1.41E-06)	D	Cooke et al., 1984
			Benzo(e)pyrene	2.93E-06 (3.52E-07)	D	Cooke et al., 1984

TABLE 4.1.2-13. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1000 gal (kg/1000 l) <sup>a</sup>	Emission Factor Rating	Reference
1-05-001-13, 1-05-002-13 (continued)	Space Heater - Atomizing Burner (continued)	None	Coronene	5.86E-06 (7.04E-07)	D	Cooke et al., 1984
			Perylene	3.52E-05 (4.22E-06)	D	Cooke et al., 1984

<sup>a</sup>Emission factors are in lb (kg) per 1,000 gal (1,000 l) of waste oil fired.

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EPA-450/3-82-006a. pp. 3-1 to 3-19. March 1982.

## 4.2 STATIONARY INTERNAL COMBUSTION

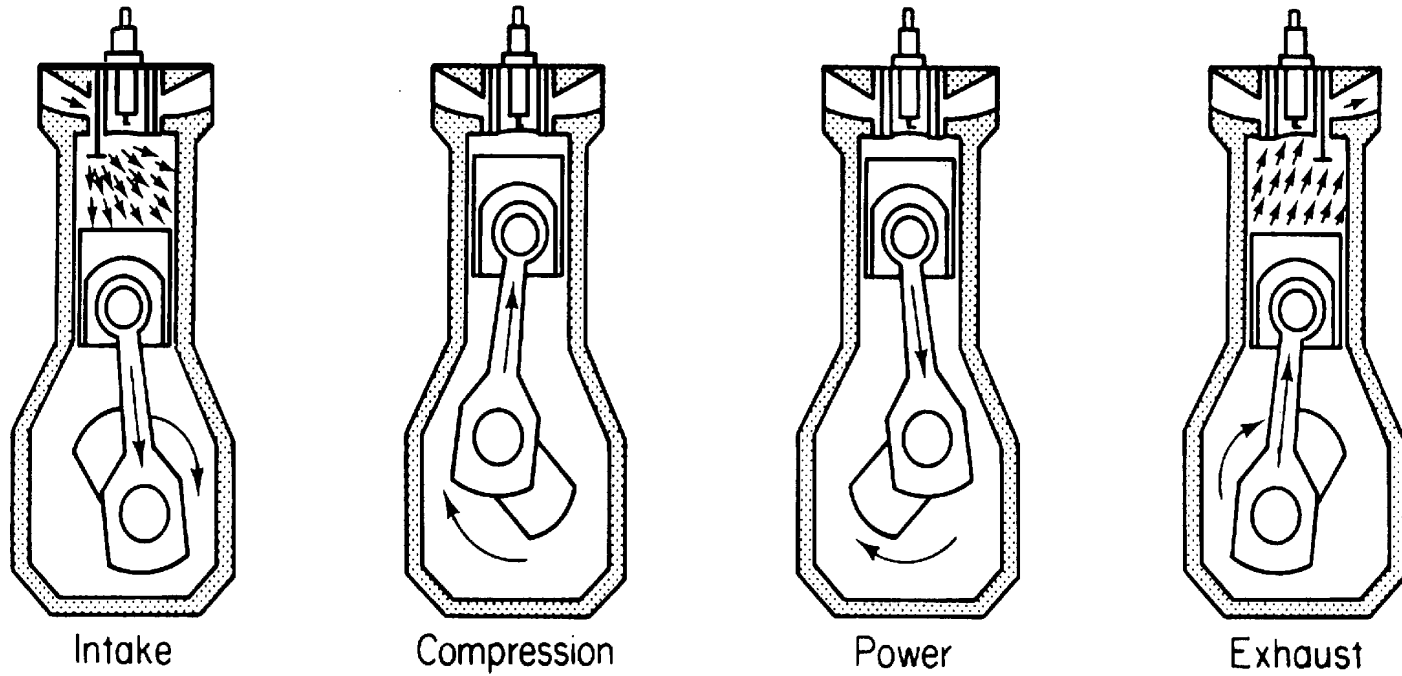
Stationary internal combustion (IC) sources are grouped into two categories: reciprocating engines and gas turbines. POM emissions primarily result from the incomplete combustion of the gasoline, diesel, or natural gas fuel that is burned in these engines and turbines. The principal application areas for stationary IC engines and turbines are electricity generation and industrial applications such as oil and gas transmission, natural gas processing, and oil and gas production and exploration (Shih et al., 1979). The use of stationary IC engines is so widespread that source locations are not listed in this document (U.S. EPA, 1995).

### 4.2.1 Reciprocating Engines

The first group of stationary IC sources, reciprocating engines, may be classified into two types: spark and compression ignition (diesel), but all reciprocating IC engines operate by the same basic process shown in Figure 4.2-1. A combustible mixture is first compressed in a small volume between the head of a piston and its surrounding cylinder. The mixture is then ignited, and the resulting high pressure products of combustion push the piston through the cylinder. This movement is converted from linear to rotary motion by a crankshaft. The piston returns, pushing out exhaust gases, and the cycle is repeated (U.S. EPA, 1995).

#### Process Description--Diesel Engines

In compression ignition engines, more commonly known as diesel engines, combustion air is first compression heated in the cylinder, and fuel is then injected into the hot air. Ignition is spontaneous as the air is above the auto-ignition temperature of the fuel. All distillate oil reciprocating engines are compression-ignited (U.S. EPA, 1995).



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Figure 4.2-1. Operating Cycle of a Conventional Reciprocating Engine

Source: Flagan and Seinfeld, 1988.

Diesel engines usually operate at a higher compression ratio (ratio of cylinder volume when the piston is at the bottom of its stroke to the volume when it is at the top) than spark-ignited engines because fuel is not present during compression; hence, there is no danger of premature auto-ignition. Because engine thermal efficiency rises with increasing pressure ratio (and pressure ratio varies directly with compression ratio), diesel engines are more efficient than spark-ignited ones. This increased efficiency is gained at the expense of poorer response to load changes and a heavier structure to withstand the higher pressures (U.S. EPA, 1995).

The primary domestic use of large stationary diesel engines (greater than 600 hp [447 kW]) is in oil and gas exploration and production. These engines, in groups of three to five, supply mechanical power to operate drilling (rotary table), mud pumping and hoisting equipment, and may also operate pumps or auxiliary power generators. Another frequent application of large stationary diesels is electricity generation for both base and standby service. Smaller uses of large diesel engines include irrigation, hoisting and nuclear power plant emergency cooling water pump operation. The category of smaller diesel engines (up to 600 hp [447 kW]) covers a wide variety of industrial applications such as aerial lifts, fork lifts, mobile refrigeration units, generators, pumps, industrial sweepers/scrubbers, material handling equipment (such as conveyors), and portable well-drilling equipment. The rated power of these engines can be up to 250 hp (186 kW), and substantial differences in engine duty cycles exist (U.S. EPA, 1995).

#### Emission Factors--Diesel Engines

Most of the pollutants from IC engines are emitted through the exhaust. However, some hydrocarbons escape from the crankcase as a result of blow-by (gases that are vented from the oil pan after they have escaped from the cylinder past the piston rings) and from the fuel tank and carburetor because of evaporation. Nearly all of the hydrocarbons from diesel engines enter the atmosphere from the exhaust. Crankcase blow-by is minor because hydrocarbons are not present during compression of the charge. Evaporative losses are insignificant in diesel engines due to the low volatility of diesel fuels. In general, evaporative losses are also negligible in engines using gaseous fuels because these engines receive their fuel continuously from a pipe rather than via a fuel storage tank and fuel pump (U.S. EPA, 1995).



Available emission factors for PAH from small uncontrolled industrial, commercial, and institutional diesel-fired IC engines are shown in Table 4.2-1. Emission factors for PAH from large stationary diesel engines (so-called “large-bore” engines) are shown as well (U.S. EPA, 1995). It must be noted that emissions can vary significantly from one engine to the next depending on its design and duty cycle.

Control measures for large stationary diesel engines to date have been directed mainly at limiting NO<sub>x</sub> emissions, because NO<sub>x</sub> is the primary pollutant from this group of IC engines. All of these controls are engine control techniques except for the selective catalytic reduction (SCR) technique, which is a post-combustion control. As such, all of these controls usually affect the emissions profile for the other pollutants such as PAH as well. The effectiveness of controls on an particular engine will depend on the specific design of each engine and the effectiveness of each technique could vary considerably. Other NO<sub>x</sub> control techniques exist and include internal/external exhaust gas recirculation (EGR), combustion chamber modification, manifold air cooling, and turbocharging. Various other emission reduction technologies may be applicable to the smaller diesel and gasoline engines. These technologies are categorized into fuel modifications, engine modifications, and exhaust after-treatments (U.S. EPA, 1995).

#### Process Description--Gasoline Engines

The other type of engine, spark ignition, initiates combustion by the spark of an electrical discharge. The fuel may be mixed with the air in a carburetor, or the fuel can be injected into the compressed air in the cylinder. All gasoline reciprocating engines are spark-ignited. Gasoline engines up to 600 hp (447 kW) can be used interchangeably with diesel IC engines in the same industrial applications described previously. As with diesel engines, substantial differences in gasoline engine duty cycles exist, and emission profiles may be expected to differ as well (U.S. EPA, 1995). No emission factors for gasoline-fired stationary IC engines were identified.

TABLE 4.2-1. PAH EMISSION FACTORS FOR STATIONARY DIESEL  
INTERNAL COMBUSTION ENGINES - RECIPROCATING

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating
2-02-001-02, 2-03-001-01	Industrial, Commercial, and Institutional Engines	Uncontrolled	Benz(a)anthracene	1.68E-06 (7.21E-07)	E
			Benzo(a)pyrene	<1.88E-07 (<8.07E-08)	E
			Benzo(k)fluoranthene	<1.55E-07 (<6.65E-08)	E
			Chrysene	3.53E-07 (1.51E-07)	E
			Dibenz(a,h)anthracene	<5.83E-07 (<2.50E-07)	E
			Indeno(1,2,3-cd)pyrene	<3.75E-07 (<1.61E-07)	E
			Acenaphthene	<1.24E-06 (<6.09E-07)	E
			Acenaphthylene	<5.06E-06 (<2.10E-06)	E
			Anthracene	1.87E-06 (8.02E-07)	E
			Benzo(ghi)perylene	<4.89E-07 (<2.10E-07)	E
			Fluoranthene	7.61E-06 (3.26E-06)	E
Fluorene	2.92E-05 (1.25E-05)	E			

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(continued)

TABLE 4.2-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating
2-02-001-02, 2-03-001-01 (continued)	Industrial, Commercial, and Institutional Engines (continued)	Uncontrolled (continued)	Benzo(b)fluoranthene	<9.91E-08 (<4.25E-08)	E
2-02-004-01	Industrial Large Bore Engine	Uncontrolled	Benzo(a)anthracene	6.22E-07 (2.67E-07)	E
			Benzo(a)pyrene	<2.57E-07 (<1.10E-07)	E
			Benzo(k)fluoranthene	<2.18E-07 (<9.35E-08)	E
			Chrysene	1.53E-06 (6.56E-07)	E
			Dibenz(a,h)anthracene	<3.46E-07 (<1.48E-07)	E
			Indeno(1,2,3-cd)pyrene	<4.14E-07 (<1.78E-07)	E
			Acenaphthene	4.68E-06 (2.01E-06)	E
			Acenaphthylene	9.23E-06 (3.96E-06)	E
			Anthracene	1.23E-06 (5.28E-07)	E
			Benzo(ghi)perylene	<5.56E-07 (<2.39E-07)	E
			Fluoranthene	4.03E-06 (1.73E-06)	E

TABLE 4.2-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating
2-02-004-01 (continued)	Industrial Large Bore Engine (continued)	Uncontrolled (continued)	Fluorene	1.28E-05 (5.49E-05)	E
			Naphthalene	0.00013 (5.58E-05)	E
			Phenanthrene	4.08E-05 (1.75E-05)	E
			Pyrene	3.71E-06 (1.59E-06)	E
			Benzo(b)fluoranthene	1.11E-06 (4.76E-07)	E

<sup>a</sup>Emission factors in lb/MMBtu (g/MJ) of heat input.

Source: U.S. EPA, 1995.

## Process Description--Natural Gas Engines

Most reciprocating IC engines that use natural gas are of the spark-ignited type. As with gasoline engines, the gas is first mixed with the combustion air at an intake valve, but the fuel may also be injected into the compressed air in the cylinder. Natural gas can be used in a compression ignition engine but only if a small amount of diesel fuel is injected into the compressed air/gas mixture to initiate combustion, hence the name dual-fuel engine. Dual-fuel engines were developed to obtain compression ignition performance and the economy of natural gas, using a minimum of 5 to 6 percent diesel fuel to ignite the natural gas. Large dual-fuel engines have been used almost exclusively for prime electric power generation (U.S. EPA, 1995).

Natural gas-fired stationary IC engines are also used in the natural gas industry primarily to power compressors used for pipeline transportation, field gathering (collecting gas from wells), underground storage, and gas processing plant applications, collectively referred to as prime movers. Pipeline engines are concentrated in the major gas-producing states (such as those along the Gulf Coast) and along the major gas pipelines (U.S. EPA, 1995).

Reciprocating IC engines used in the natural gas industry are separated into three design classes: two-stroke lean burn, four-stroke lean burn, and four-stroke rich burn. Two-stroke engines complete the power cycle in a single engine revolution compared to two revolutions for four-stroke engines. Four-stroke engines use a separate engine revolution for the intake/compression stroke and the power/exhaust stroke. Both types of engines may be turbocharged using an exhaust-powered turbine to pressurize the charge for injection into the cylinder (U.S. EPA, 1995). Rich-burn engines operate near the fuel/air stoichiometric limit with exhaust excess oxygen levels less than 4 percent. Lean-burn engines may operate up to the lean flame extinction limit, with exhaust oxygen levels of 12 percent or greater (U.S. EPA, 1995).

Pipeline population statistics show a nearly equal installed capacity of reciprocating IC engines and gas turbines (which are discussed in Section 4.2.2). For

reciprocating engines, two-stroke designs contribute approximately two-thirds of installed capacity in this industry (U.S. EPA, 1995).

#### Emission Factors--Natural Gas Engines

Emission factors for PAH from two uncontrolled natural gas-fired reciprocating engines--one two-stroke and one four-stroke--are listed in Table 4.2-2 (Meeks, 1992).

Because  $\text{NO}_x$  is the primary pollutant of significance emitted from natural gas-fired engines, control measures to date have been directed mainly at limiting  $\text{NO}_x$  emissions. Here again, the  $\text{NO}_x$  control measures often affect the emissions of other pollutants, and not always positively. New applications of dry low  $\text{NO}_x$  combustor can designs and selective catalytic reduction (SCR) are appearing (U.S. EPA, 1995).

#### 4.2.2 Gas Turbines

##### Process Description

The second group of stationary internal combustion sources, gas turbines, are so named not because they are gas-fired, but because combustion exhaust gas drives the turbine. Unlike the reciprocating engines, the gas turbine operates in steady flow. As shown in Figure 4.2-2, a basic gas turbine consists of a compressor, a combustor, and a turbine. Combustion air enters the turbine through a centrifugal compressor, where the pressure is raised to 5 to 30 atm, depending on load and the design of the engine. Part of the air is then introduced into the primary combustion zone, into which fuel is sprayed and burns in an intense flame. The gas volume increases with combustion, so as the gases pass at high velocity through the turbine, they generate more work than is required to drive the compressor. This additional work is delivered by the turbine to a shaft, to drive an electric power generator or other machinery (Flagan and Seinfeld, 1988).

TABLE 4.2-2. PAH EMISSION FACTORS FOR STATIONARY NATURAL GAS-FIRED  
INTERNAL COMBUSTION ENGINES - RECIPROCATING

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMCF (kg/MMm <sup>3</sup> ) <sup>a</sup>	Emission Factor Rating
2-02-002-52	Two-Cycle Lean Burn	Uncontrolled	Benz(a)anthracene	4.10E-04 (6.54E-03)	E
			Benzo(a)pyrene	4.16E-04 (6.64E-03)	E
			Benzo(b)fluoranthene	7.30E-05 (1.16E-03)	E
			Benzo(k)fluoranthene	2.56E-03 (0.0408)	E
			Chrysene	8.04E-04 (0.0128)	E
			Dibenz(a,h)anthracene	3.68E-05 (5.87E-04)	E
			Indeno(1,2,3-cd)pyrene	6.40E-05 (1.02E-03)	E
			Acenaphthene	3.38E-04 (5.39E-03)	E
			Acenaphthylene	5.00E-03 (0.0798)	E
			Anthracene	2.07E-03 (0.0330)	E
			Benzo(ghi)perylene	4.44E-05 (7.08E-04)	E
Fluoranthene	8.32E-05 (1.33E-03)	E			

TABLE 4.2-2. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMCF (kg/MMm <sup>3</sup> ) <sup>a</sup>	Emission Factor Rating
2-02-002-52 (continued)	Two-Cycle Lean Burn (continued)	Uncontrolled (continued)	Fluorene	1.11E-03 (0.0177)	E
			Naphthalene	0.111 (1.77)	E
			Phenanthrene	2.29E-03 (0.0365)	E
			Pyrene	1.16E-04 (1.85E-03)	E
2-02-002-53	Four-Cycle Rich Burn	Uncontrolled	Benz(a)anthracene	7.47E-05 (1.19E-03)	E
			Benzo(a)pyrene	3.42E-05 (5.45E-04)	E
			Benzo(b)fluoranthene	2.91E-04 (4.64E-03)	E
			Benzo(k)fluoranthene	5.24E-04 (8.36E-03)	E
			Chrysene	9.20E-05 (1.47E-03)	E
			Dibenz(a,h)anthracene	1.03E-05 (1.64E-04)	E
			Indeno(1,2,3-cd)pyrene	1.15E-04 (1.83E-03)	E
			Acenaphthene	6.92E-04 (0.0110)	E



TABLE 4.2-2. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMCF (kg/MMm <sup>3</sup> ) <sup>a</sup>	Emission Factor Rating
2-02-002-53 (continued)	Four-Cycle Rich Burn (continued)	Uncontrolled (continued)	Acenaphthylene	7.42E-03 (0.118)	E
			Anthracene	2.46E-04 (3.92E-03)	E
			Benzo(ghi)perylene	9.94E-05 (1.59E-03)	E
			Fluoranthene	2.39E-04 (3.81E-03)	E
			Fluorene	4.43E-04 (7.07E-03)	E
			Naphthalene	0.117 (1.87)	E
			Phenanthrene	8.57E-04 (0.0137)	E
			Pyrene	1.17E-04 (1.87E-03)	E

<sup>a</sup>Emission factors in lb per million cubic feet, lb/MMCF (kg per million cubic meters, kg/MMm<sup>3</sup>) of natural gas fired.

Source: Meeks, 1992.

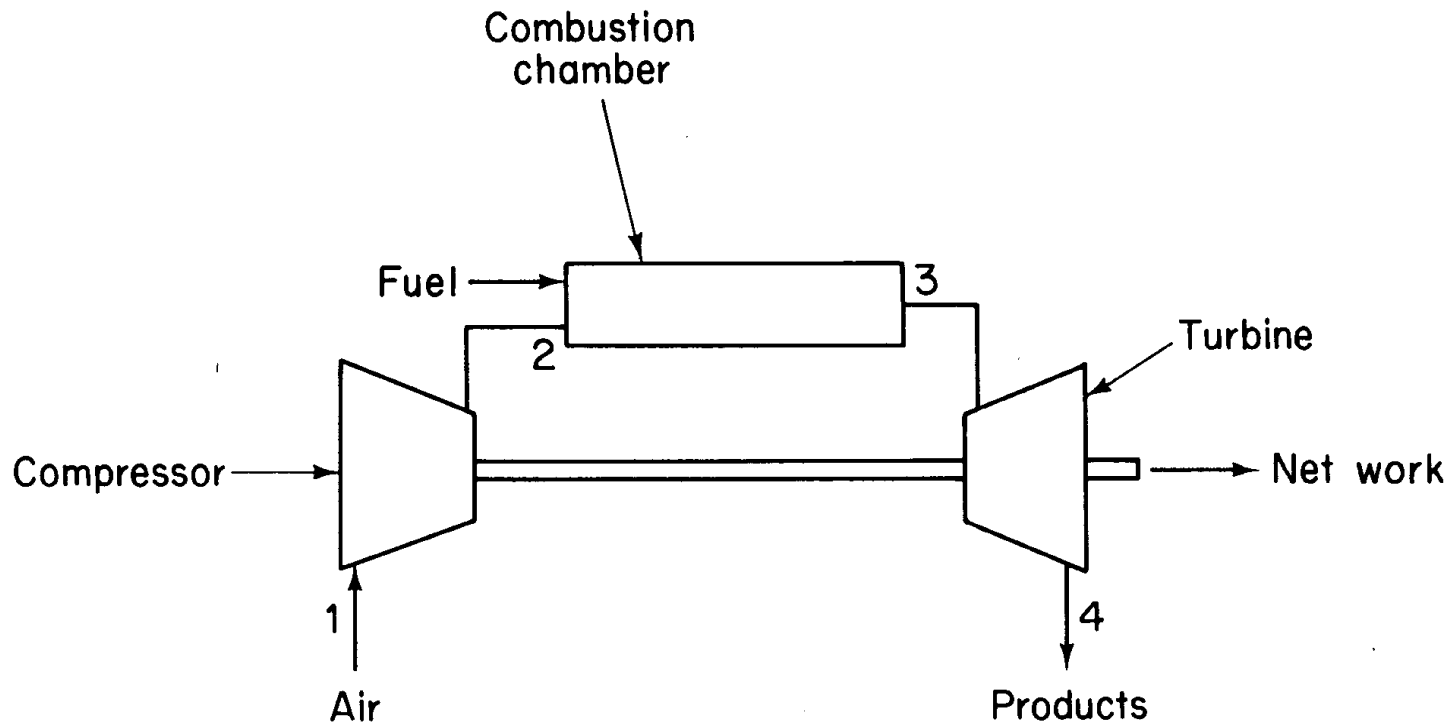


Figure 4.2-2. Gas Turbine Engine Configuration

Source: Flagan and Seinfeld, 1988.

Gas turbines may be classified into three general types: simple open cycle, regenerative open cycle, and combined cycle. In the simple open cycle, the hot gas discharged from the turbine is exhausted to the atmosphere. In the regenerative open cycle, the gas discharged from the turbine is passed through a heat exchanger to preheat the combustion air. Preheating the air increases the efficiency of the turbine. In the combined cycle, the gas discharged from the turbine is used as auxiliary heat for a steam cycle. Regenerative-type gas turbines constitute only a very small fraction of the total gas turbine population. Identical gas turbines used in the combined cycle and in the simple cycle tend to exhibit the same emissions profiles. Therefore, usually only emissions from simple cycles are evaluated (Shih et al., 1979).

The same fuels used in reciprocating engines are combusted to drive gas turbines. The primary fuels used are natural gas and distillate (No. 2) fuel oil, although residual fuel oil is used in a few applications (U.S. EPA, 1995). The liquid fuel used must be similar in volatility to diesel fuel to produce droplets that penetrate sufficiently far into the combustion chamber to ensure efficient combustion even when a pressure atomizer is used (Flagan and Seinfeld, 1988).

Stationary gas turbines are applied in electric power generators, in gas pipeline pump and compressor drives, and in various process industries. Gas turbines [greater than 3 MW(e)] are used in electrical generation for continuous, peaking, or standby power (U.S. EPA, 1995). In 1990, the actual gas-fired combustion turbine generating capacity for electric utilities was 8,524 MW (NAERC, 1991). The current average size of electricity generation gas turbines is approximately 31 MW. Turbines are also used in industrial applications, but information was not available to estimate their installed capacity.

### Emission Factors

Emission control technologies for gas turbines have advanced to a point where all new and most existing units are complying with various levels of specified emission limits. Today most gas turbines are controlled to meet local, State, and/or Federal regulations. For these sources, emission factors have become an operational specification rather than a parameter to be quantified by testing (U.S. EPA, 1995). As with reciprocating engines, the primary pollutant

from gas turbines is  $\text{NO}_x$ , and techniques for its control still have ramifications for the emissions profiles of other pollutants such as PAHs. Available PAH emission factors for diesel- and natural gas-fired gas turbines are listed in Table 4.2-3 (Carnot, 1989; Carnot, 1990; U.S. EPA, 1995).

Water/steam injection is the most prevalent  $\text{NO}_x$  control for co-generation/combined cycle gas turbines. The water or steam is injected with the air and fuel into the turbine combustor in order to lower the peak temperatures, which in turn decreases the thermal  $\text{NO}_x$  produced. The lower average temperature within the combustor can may produce higher levels of CO and hydrocarbons as a result of incomplete combustion (U.S. EPA, 1995). SCR systems can be used also, all existing applications of SCR have been used in conjunction with water/steam injection controls (U.S. EPA, 1995).

TABLE 4.2-3. PAH EMISSION FACTORS FOR STATIONARY INTERNAL COMBUSTION ENGINES - GAS TURBINES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ) <sup>a</sup>	Emission Factor Rating	Reference
2-01-001-01	Electric Generation, Diesel-Fired	Afterburner	Anthracene	<3.43E-08 (<1.47E-08)	E	Carnot, 1990
			Fluorene	<2.56E-08 (<1.10E-08)	E	Carnot, 1990
			Phenanthrene	<5.87E-08 (<2.52E-08)	E	Carnot, 1990
2-01-001-01	Electric Generation, Diesel-Fired	Steam or Water Injection	Phenanthrene	<2.69E-08 (<1.15E-08)	E	Carnot, 1989
2-01-002-01	Electric Generation, Natural Gas-Fired	Selective Catalytic Reduction	Naphthalene	<4.9E-05 (<2.10E-05)	E	U.S. EPA, 1995

<sup>a</sup>Emission factors in lb/MMBtu (g/MJ) of heat input.

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## 4.3 WASTE INCINERATION

### 4.3.1 Municipal Waste Combustion

#### Process Description

Municipal waste combustors (MWCs) burn garbage and other nonhazardous solid waste, commonly called municipal solid waste (MSW). Three main design types of technologies are used to combust MSW: mass burn, refuse-derived fuel-fired (RDF), and modular combustors.

Mass Burn Combustors--In mass burn units, the MSW is combusted without any preprocessing other than removal of items too large to go through the feed system. In a typical mass burn combustor, refuse is placed on a grate that moves through the combustor. Combustion air in excess of stoichiometric amounts is supplied both below (underfire air) and above (overfire air) the grate. Mass burn combustors are usually erected at the site (as opposed to being prefabricated at another location), and range in size from 50 to 1,000 tons/day (46 to 900 Mg/day) of MSW throughput per unit. Mass burn combustors can be divided into mass burn/waterwall (MB/WW), mass burn/rotary waterwall combustor (MB/RC), and mass burn refractory wall (MB/REF) designs.

MB/WW combustor walls are constructed of metal tubes that contain pressurized water and recover radiant heat for production of steam and/or electricity. A typical MB/WW combustor is shown in Figure 4.3.1-1. With the MB/RC, a rotary combustion chamber sits at a slight angle and rotates at about 10 revolutions per hour, causing the waste to advance and tumble as it burns. The combustion cylinder consists of alternating water tubes and perforated steel plates. An MB/RC combustor normally operates at about 50 percent excess air. Figure 4.3.1-2 illustrates a simplified process flow diagram for a MB/RC. MB/REF designs are older and typically do not include any heat recovery. One type of MB/REF combustor is shown in Figure 4.1.3-3.

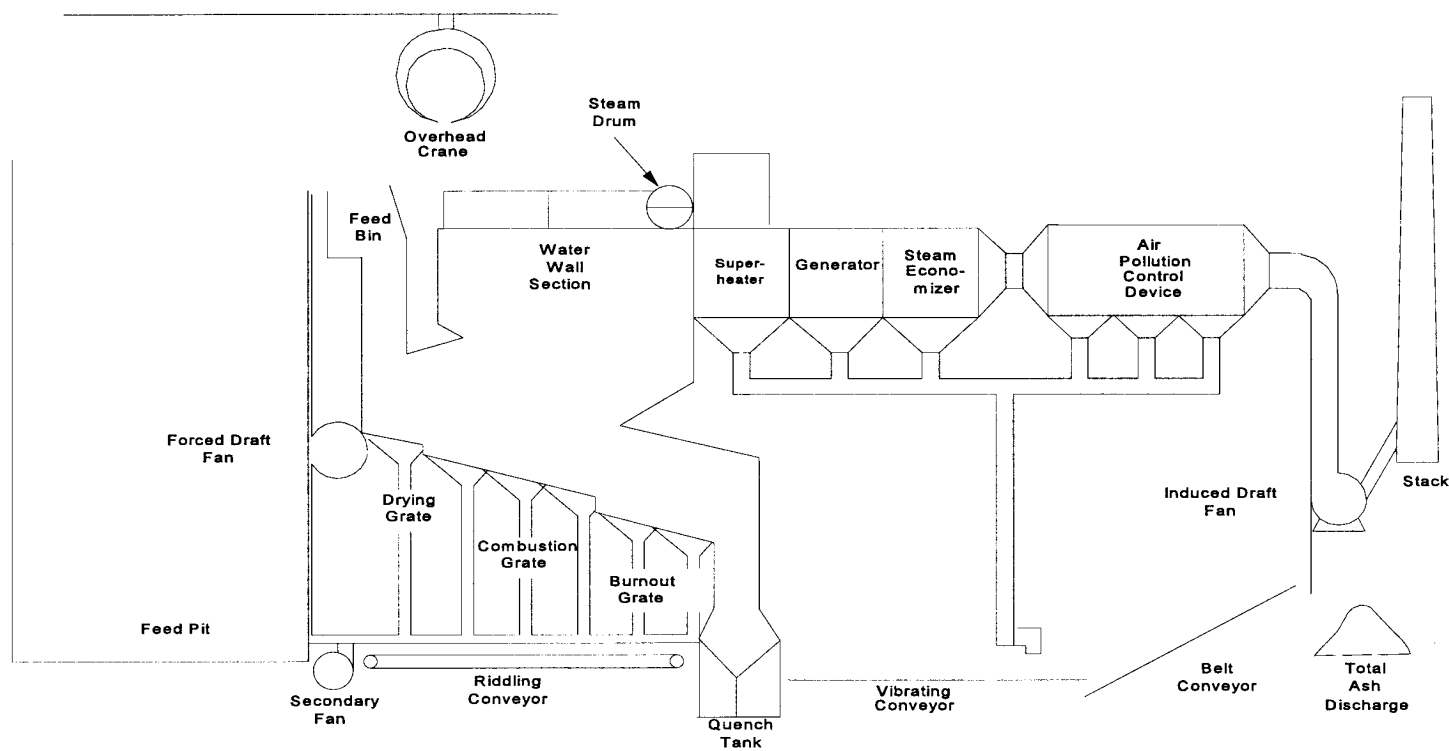


Figure 4.3.1-1. Typical Mass Burn Waterwall Combustor

Source: U.S. EPA, 1993.



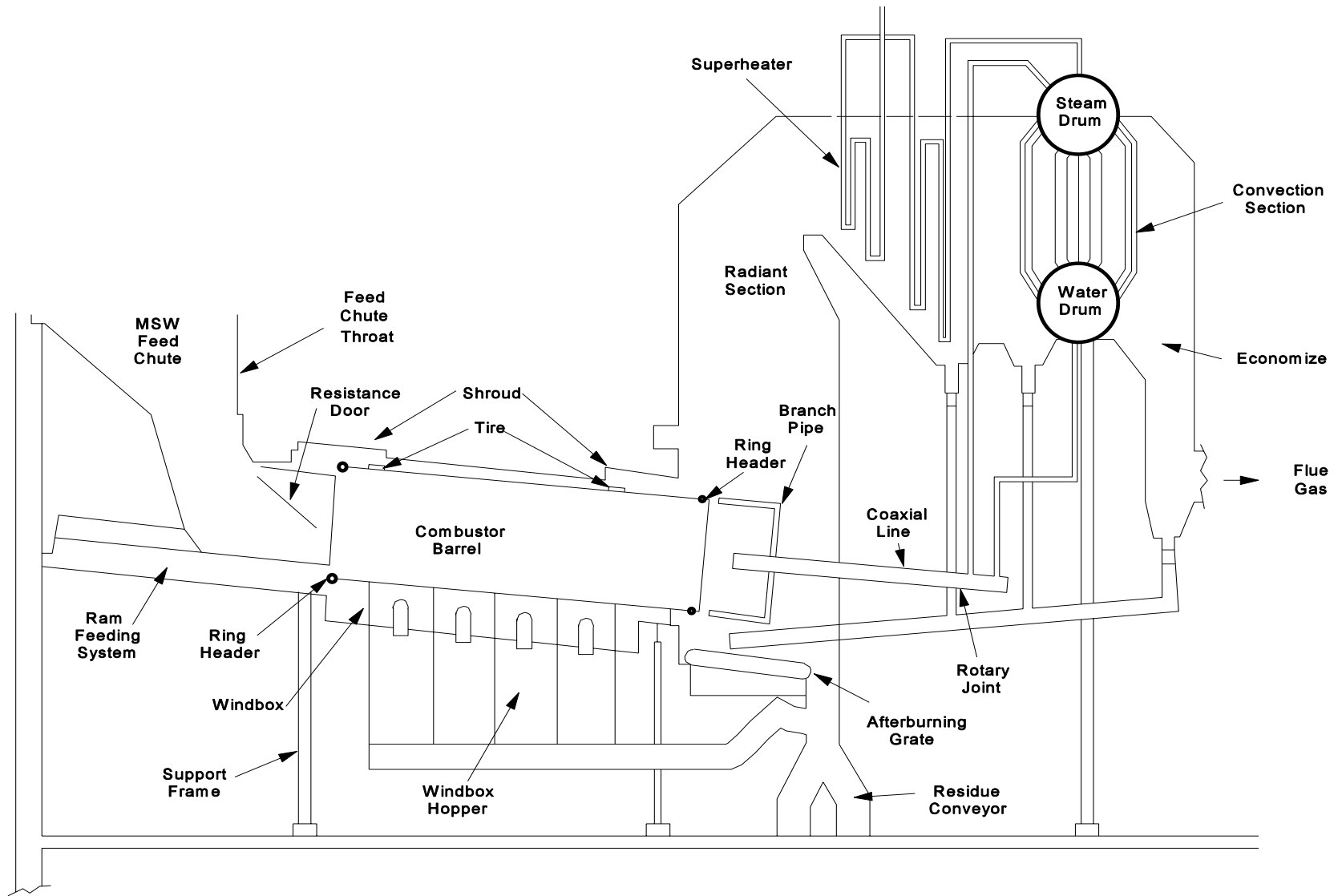


Figure 4.3.1-2. Simplified Process Flow Diagram, Gas Cycle for a Mass Burn/Rotary Waterwall Combustor

Source: U.S. EPA, 1993.

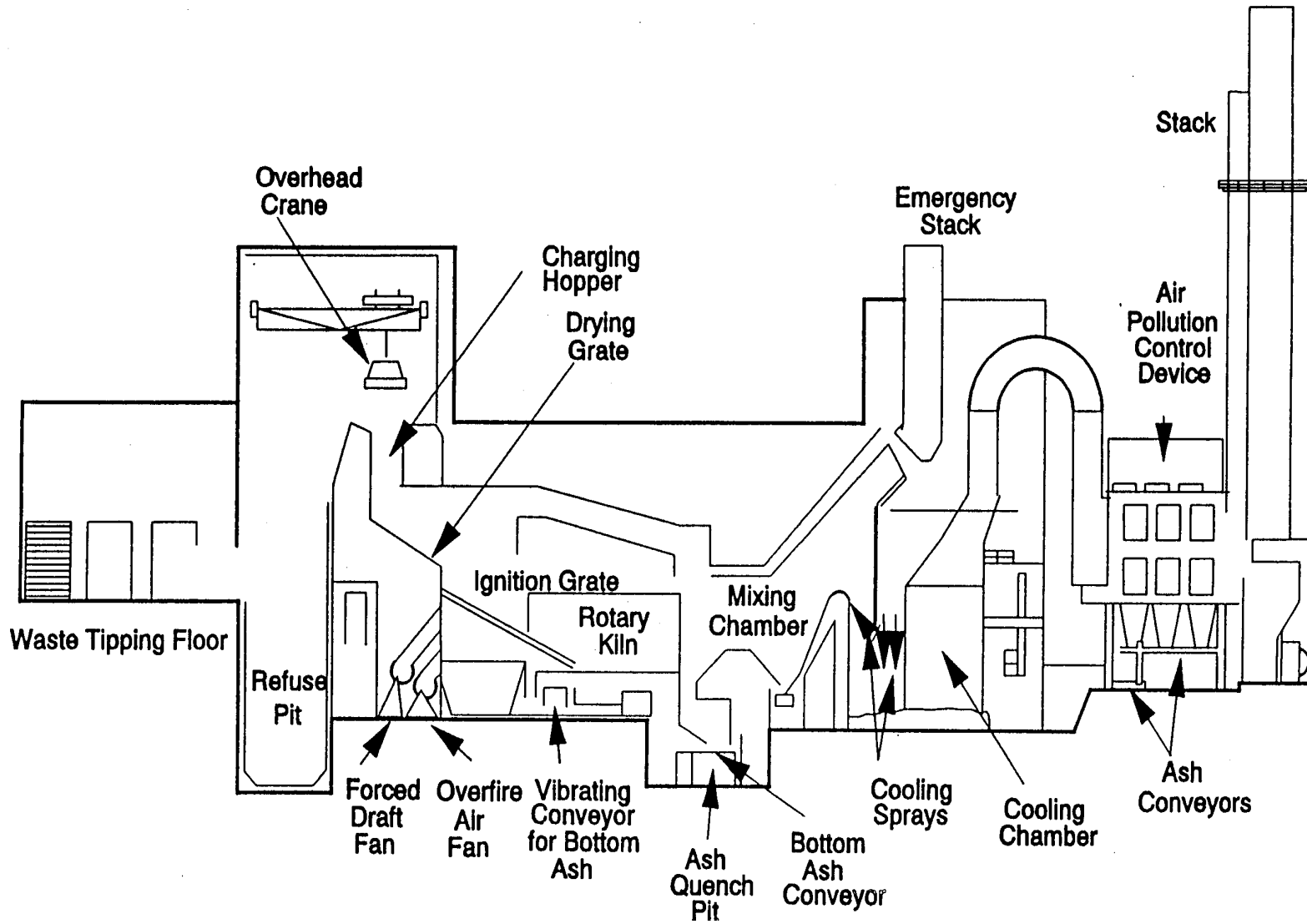


Figure 4.3.1-3. Mass Burn Refractory-Wall Combustor with Grate/Rotary Kiln

Source: U.S. EPA, 1993.

RDF-fired Combustors--RDF combustors burn processed waste that varies from shredded waste to finely divided fuel suitable for co-firing with pulverized coal. Combustor sizes range from 320 to 1,400 tons/day (290 to 1,300 Mg/day). There are three major types of RDF-fired combustors: (1) dedicated RDF combustors, which are designed to burn RDF as a primary fuel, (2) coal/RDF co-fired, and (3) fluidized-bed combustors (FBCs) where waste is combusted on a turbulent bed of limestone, sand, silica or aluminum. A typical RDF-fired combustor is shown in Figure 4.3.1-4. Waste processing usually consists of removing noncombustibles and shredding, which generally raises the heating value and provides a more uniform fuel. The type of RDF used depends on the boiler design. Most boilers designed to burn RDF use spreader stokers and fire fluff RDF in a semi-suspension mode.

Modular Combustors--Modular combustors are similar to mass burn combustors in that they burn waste that has not been pre-processed, but they are typically shop fabricated and generally range in size from 5 to 140 tons/day (4 to 130 Mg/day) of MSW throughput. One of the most common types of modular combustors is the starved-air or controlled-air type, which incorporates two combustion chambers. A process diagram of a typical modular starved-air (MOD/SA) combustor is presented in Figure 4.3.1-5. Air is supplied to the primary chamber at sub-stoichiometric levels. The incomplete combustion products (CO and organic compounds) pass into the secondary combustion chamber, where additional air and fuel are added and combustion is completed. Another type of design is the modular excess air (MOD/EA) combustor that consists of two chambers, similar to MOD/SA units, but is functionally like the mass burn unit in that it uses excess air in the primary chamber.

Emissions of PAH from municipal incinerators are suspected to occur primarily from incomplete combustion of non-PAH carbonaceous material or high-temperature free radical mechanisms (WHO, 1988). It is unlikely that PAHs in the refuse feed material persist throughout the combustion process. It is estimated that PAHs account for less than 1 percent of the total organic carbon (TOC) in the products of incineration.

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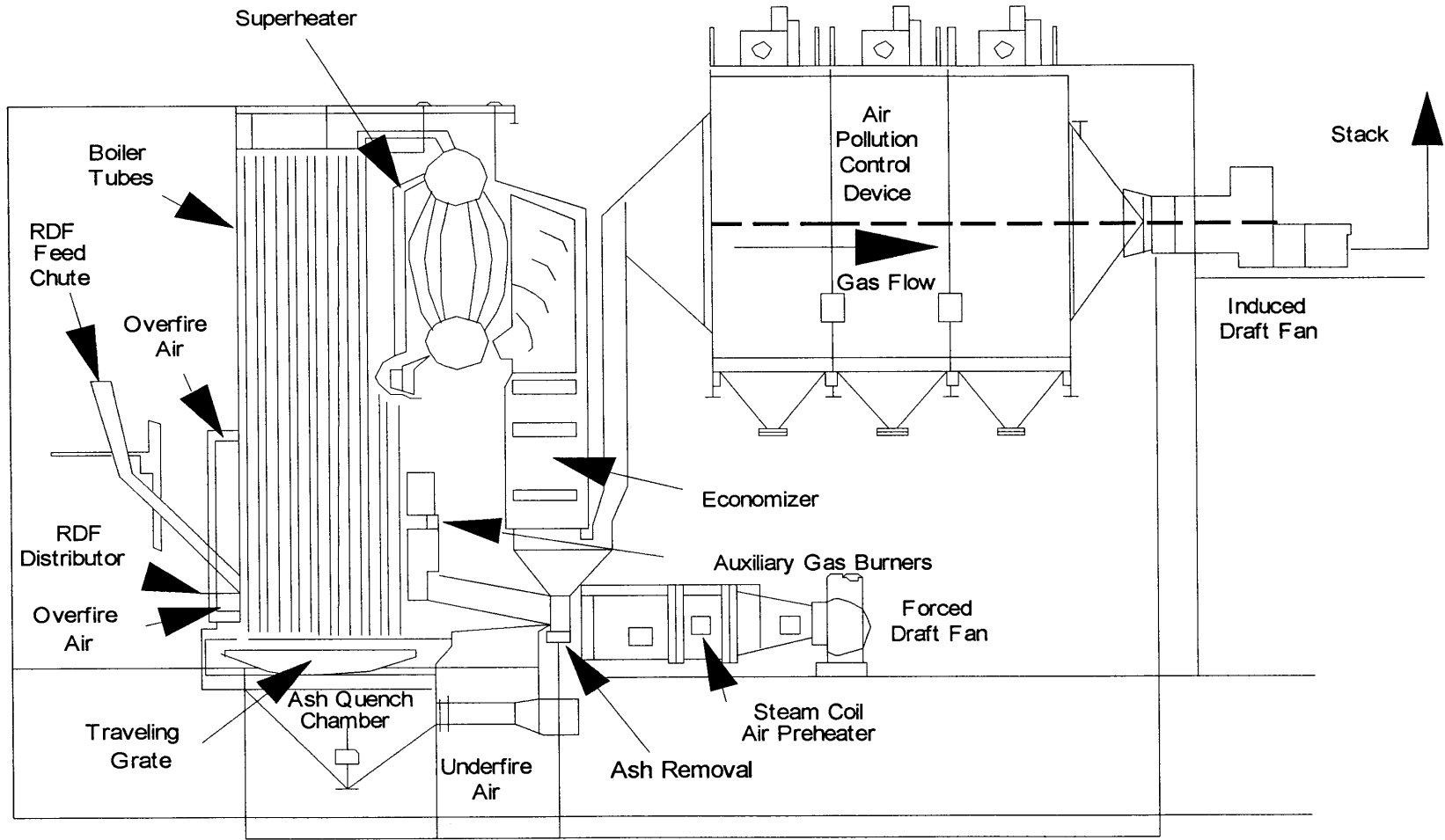


Figure 4.3.1-4. Typical RDF-Fired Spreader Stoker Boiler

Source: U.S. EPA, 1993.

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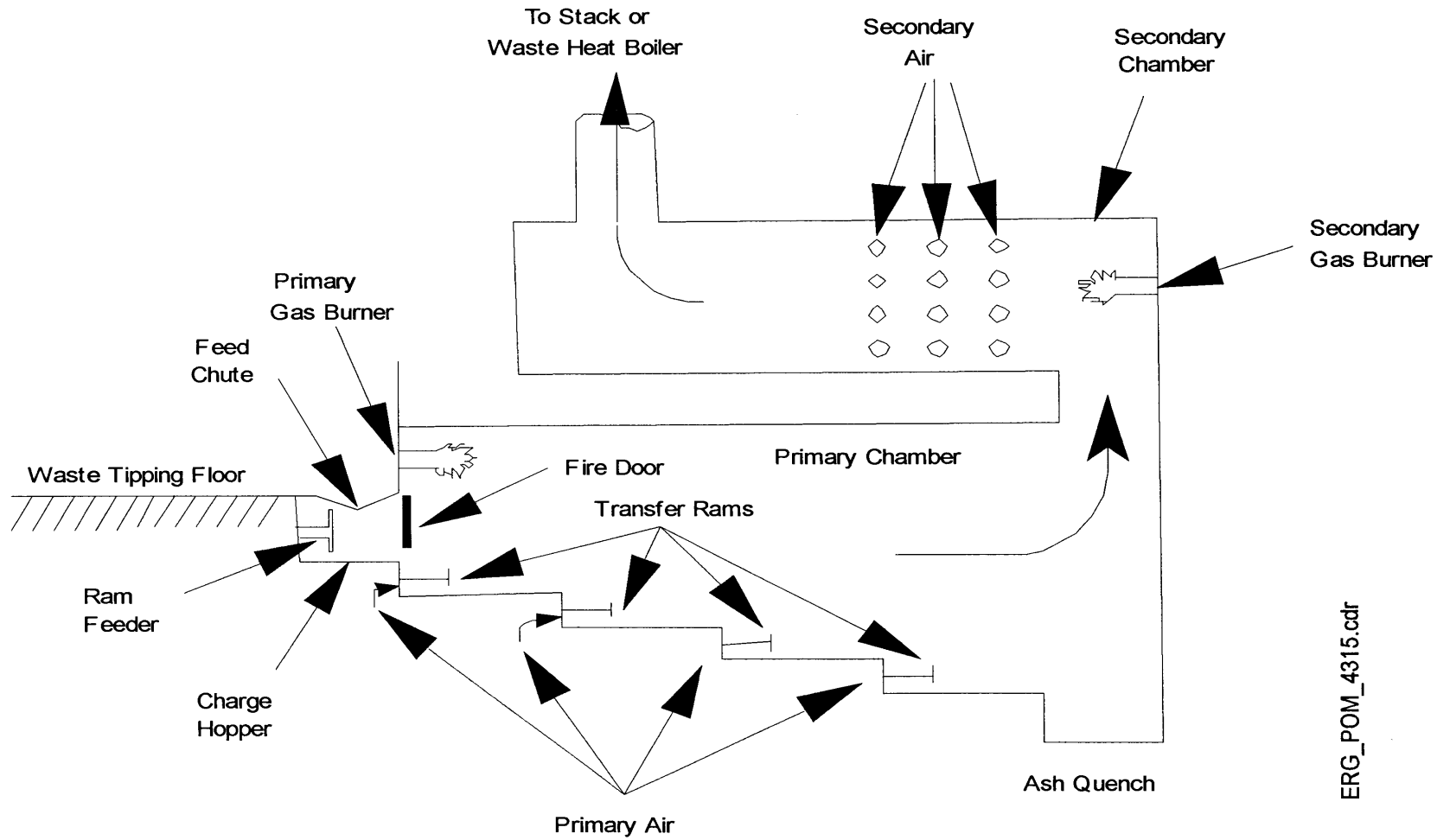


Figure 4.3.1-5. Typical Modular Starved-Air Combustor with Transfer Rams

Source: U.S. EPA, 1993.

Failure to achieve complete combustion of the organic materials evolved from the waste can result in emissions of a variety of organic compounds, including PAH. In general, adequate oxygen, temperature, residence time, and turbulence will minimize emissions of most organics. Tests show that advanced incinerators operating at sufficiently high temperatures and with adequate oxygen, good mixing, and adequate retention time result in lower formation levels of PAH than in traditional and poorly maintained or operated incinerators (WHO, 1988).

Emission Control Techniques--There are basically three methods to controlling emissions from MWCs. These methods can be applied separately or in combination. The first method involves separation of materials for recovery prior to combustion. The result of recovering certain materials instead of combusting them is a reduction in the amount of waste combusted and in the amount of pollutants emitted (Federal Register, 1989).

Another method of controlling MWC emissions is to alter the combustion process to reduce emissions of organics, including PAH. This method is referred to as Good Combustion Practices (GCP). Good combustion practices include the proper design, construction, operation, and maintenance of an MWC. The use of GCP reduces MWC organic emissions by promoting more thorough combustion of these pollutants. Important elements of GCP include (Federal Register, 1989).

- Maintaining uniform waste feed rates and conditions;
- The use of preheated air to combust wet or difficult to combust materials;
- Maintaining adequate combustor temperature and residence time;
- Providing proper total combustion (excess) air levels;
- Supplying proper amounts of primary (underfire) and secondary (overfire) air;
- Minimizing PM carryover;
- Monitoring the degree of waste burnout; and

- The use of auxiliary fuel during startup and shutdown.

The third method of controlling MWC emissions is adding pollution control equipment after the MWC. The most frequently used control devices for MWCs are combinations of spray dryers and ESPs, or spray dryers and fabric filters (FF). Spray drying was initially developed to control acid gas emissions. However, spray drying also controls MWC organic emissions, including PAHs. Fabric filters and ESPs control particulate matter emissions and, therefore, particle-associated PAH (Federal Register, 1989).

#### Emission Factors

A search for MWC PAH emissions data produced information for the following types of MWCs and control devices:

- Single chamber, reciprocating grate with ESP (Haile et al., 1984);
- Single chamber, fluidized bed, uncontrolled (Yasuda and Kaneko, 1989);
- Multiple chamber, rocking bar grate with wet scrubber and ESP (Shih et al., 1980);
- Mass burn waterwall, reciprocating grate with ESP (MRI, 1987);
- Multiple chamber with ESP (AmTest, Inc., 1989);
- Multiple chamber, RDF with ESP (MRI, 1987);
- Modular, starved-air, uncontrolled (U.S. EPA, 1989);
- Modular, excess-air, with ESP (U.S. EPA, 1989);
- Mass burn waterwall with spray dryer and fabric filter (IWSA, 1996); and
- Mass burn waterwall with spray dryer and ESP (IWSA, 1996).

The data obtained from the Integrated Waste Services Association (IWSA) was used to develop PAH emission factors for MWCs because most of the MWC capacity in the United States is at facilities of the types described in the data. Seventy percent of the MWC capacity in the United States is at mass burn facilities (Bevington, et al., 1995). Also, the majority of MSW is combusted at facilities subject to the MWC MACT, which requires that spray dryers and ESPs or spray dryers and fabric filters be used as emission controls.

Evaluation of the IWSA data shows that naphthalene was the only PAH detected, although the 16 PAHs were targeted. The other 15 PAHs were not detected in any sampling run at any facility. Thus, naphthalene was the only PAH for which an emission factor was developed. The factors for the facilities equipped with spray dryers and ESPs were not significantly different in value from the factors for facilities equipped with spray dryers and fabric filters. Therefore, the factors from both types of facilities were averaged together to obtain the factor presented in Table 4.3.1-1.

#### Source Location

As of March 1995, there were roughly 130 MWC plants operating or under construction in the United States with capacities greater than 40 tons/day (36 Mg/day), with a total national capacity of approximately 103,300 tons/day (93,909 Mg/day) of MSW. Of the total MWC capacity in the United States, 70 percent is at mass burn facilities, 25 percent is at RDF facilities, 4 percent is at modular facilities, and the remaining 1 percent is at other technology facilities such as co-fired RDF combustors. Ninety-one percent of the MWC facilities (99 percent of MWC capacity) employ air emission controls of some kind (Bevington et al., 1995). Table 4.3.1-2 lists the geographical distribution of these MWC units and their statewide capacities (Bevington et al., 1995).



TABLE 4.3.1-1. PAH EMISSION FACTORS FOR MUNICIPAL WASTE COMBUSTION SOURCES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
5-01-001-05	Mass Burn, Water Wall Combustor	Spray Dryer and Fabric Filter, or Spray Dryer and ESP	Naphthalene	6.06E-06 (3.04)	4.81E-07 - 1.46E-05 (2.40E-01 - 7.29)	C	IWSA, 1996

<sup>a</sup>Emission factors are expressed in lb (mg) of pollutant emitted per ton (Mg) of waste incinerated.

TABLE 4.3.1-2. SUMMARY OF GEOGRAPHICAL DISTRIBUTION  
OF MWC FACILITIES<sup>a</sup>

State	Number of MWC Facilities	State MWC Capacity in tons/day (Mg/day)	Percentage of Total MWC Capacity in the United States
AK	2	120 (109)	<1
AL	1	690 (627)	<1
AR	4	283 (257)	<1
CA	3	2,560 (2,330)	2
CT	7	6,545 (5,950)	6
FL	14	18,248 (16,589)	17
GA	1	500 (450)	<1
HI	1	2,160 (1,964)	2
ID	1	50 (45)	<1
IL	1	1,600 (1,450)	1
IN	1	2,360 (2,150)	2
MA	11	11,003 (10,003)	10
MD	4	5,910 (5,373)	5
ME	4	2,000 (1,818)	2
MI	7	5,225 (4,750)	5

TABLE 4.3.1-2. (Continued)

State	Number of MWC Facilities	State MWC Capacity in tons/day (Mg/day)	Percentage of Total MWC Capacity in the United States
MN	12	5,102 (4,638)	5
MS	1	150 (140)	<1
MT	1	72 (65)	<1
NC	5	1,324 (1,204)	1
NH	3	832 (756)	1
NJ	6	5,820 (5,290)	6
NY	13	11,545 (10,496)	11
OH	6	1,800 (1,636)	2
OK	2	1,230 (1,120)	1
OR	2	675 (614)	1
PA	7	8,702 (7,911)	8
SC	2	870 (791)	1
TN	2	1,250 (1,136)	1
TX	3	195 (177)	<1
UT	1	400 (360)	<1

TABLE 4.3.1-2. (Continued)

State	Number of MWC Facilities	State MWC Capacity in tons/day (Mg/day)	Percentage of Total MWC Capacity in the United States
VA	6	6,325 (5,750)	6
WA	5	1,500 (1,360)	1
WI	4	831 (755)	1

<sup>a</sup>List of facilities represents the plants in operation or under construction/modification that are expected to be subject to the MACT standards being developed for MWCs.

Source: Bevington et al., 1995.

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#### 4.3.2 Industrial and Commercial Waste Incineration

##### Process Description

In addition to municipal waste incinerators, some solid waste is also incinerated in industrial and commercial facilities. Most individual waste incinerators at these sites are subject to State and local air quality regulations such that these units have varying degrees of emissions control. Most are equipped with afterburners, and newer units may have or be required to install scrubbers or ESPs (Kelly, 1983).

Industrial wastes combusted in incinerators consist primarily of processing wastes and plant refuse and contain paper, plastic, rubber, textiles, and wood. Because of the variety of manufacturing operations, waste compositions are highly variable between plants, but may be fairly consistent within a plant. Industrial waste incinerators are basically the same design as municipal waste incinerators. Available data indicate that approximately 91 percent of the units are multichamber designs, 8 percent are single chamber designs, and 1 percent are rotary kiln or fluidized bed designs. About 1,500 of the estimated 3,800 industrial incinerators are used for volume reduction, 640 units (largely in the petroleum and chemical industries) are used for toxicity reduction, and the remaining 1,700 units are used for resource recovery, primarily at copper wire and electric motor plants (Kelly, 1983).

Commercial waste incinerators are used to reduce the volume of wastes from large office and living complexes, schools, and commercial facilities. Small multichamber incinerators are typically used and over 90 percent of the units require firing of an auxiliary fuel. Emission controls are generally not present on commercial units. The inefficient methods of combustion used in the majority of commercial waste incinerators make these units potentially significant POM emission sources (Kelly, 1983).

Polycyclic organic matter emissions from industrial and commercial waste incineration are a function of waste composition, incinerator design and operating practices, and incinerator emissions control equipment. Both the incineration of wastes and the combustion of

incinerator auxiliary fuel may be sources of POM emissions. Greater organics and moisture content in wastes increase potential POM emissions upon incineration. Incinerator design and operating practices affect waste mixing, residence time in the flame zone, combustion stoichiometry, and other factors that contribute to POM emissions generation. Incinerator emission controls affect POM emissions by determining whether particulate matter and gaseous pollutants are controlled and to what extent. Generally, POM emissions exist in both particulate and gaseous forms, with available data indicating that often gaseous POM emissions predominate. Incinerators with emission controls designed primarily for particulate matter collection may be accomplishing little POM emissions control.

### Emission Factors

Available POM emission factor data for commercial waste incineration sources are given in Table 4.3.2-1 (Hangebrauck et al., 1967). There were no available emission factors for industrial waste incineration; however, to some extent this category is covered in Section 4.1.2 of this report which includes the incineration of industrial wood waste.

The test data for commercial waste incinerators in Table 4.3.2-1 indicates that POM emissions are generally greater from commercial sources than from municipal sources (disregarding differences for controls). This apparent trend is probably attributable to commercial units being operated and maintained less efficiently than municipal units, with emphasis not being given to optimizing combustion conditions and waste destruction. In both of the commercial unit tests described in the literature, pyrene and fluoranthene were consistently the predominant POM compounds measured of those analyzed.

TABLE 4.3.2-1. PAH EMISSION FACTORS FOR COMMERCIAL WASTE COMBUSTION SOURCES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating
5-02-001-02	Commercial Solid Waste Incinerator - Single Chamber	None	Benzo(a)pyrene	2.34E-04 (117.00)	E
			Anthracene	2.08E-04 (104.00)	E
			Benzo(ghi)perylene	3.97E-04 (198.00)	E
			Fluoranthene	9.72E-04 (485.00)	E
			Phenanthrene	6.19E-04 (309.00)	E
			Pyrene	1.41E-03 (706.00)	E
			Benzo(e)pyrene	1.99E-04 (99.20)	E
			Perylene	1.36E-05 (6.80)	E
			Anthanthrene	2.93E-05 (14.60)	E
			Coronene	9.28E-05 (46.30)	E
5-02-001-01	Commercial Solid Waste Incinerator - Multiple Chamber	None	Benzo(a)pyrene	1.15E-03 (573.00)	E
			Anthracene	3.81E-04 (190.00)	E
			Benzo(ghi)perylene	3.84E-03 (1918.00)	E
			Fluoranthene	1.72E-02 (8600.00)	E

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(continued)



TABLE 4.3.2-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating
5-02-001-01 (continued)	Commercial Solid Waste Incinerator - Multiple Chamber (continued)	None	Phenanthrene	2.61E-04 (130.00)	E
			Pyrene	1.86E-02 (9261.00)	E
			Benzo(e)pyrene	1.15E-03 (573.00)	E
			Perylene	2.65E-04 (132.00)	E
			Anthanthrene	3.49E-04 (174.00)	E
			Coronene	9.28E-04 (463.00)	E

<sup>a</sup>Emission factors are expressed in lb (mg) of pollutant emitted per ton (Mg) of waste incinerated.

Source: Hangebrauk et al., 1967.

## Source Location

No site specific location information is available for commercial and industrial waste incinerators. Commercial units are generally located in urbanized, metropolitan areas with large concentrations of people. Locations of industrial waste incinerators parallel those of the industries that use them for waste disposal. The lumber and wood products industries, the primary metals industry, and the printing industry are the greatest users of incinerators for waste disposal. Lumber and wood producers are primarily in the Southeast and Northwest. Primary metals plants are predominantly in the Midwest, the Mideast, and the Southwest. The printing industry has an essentially nationwide distribution (Kelly, 1983).

## SECTION 4.3.2 REFERENCES

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Kelly, M.E. Sources and Emissions of Polycyclic Organic Matter. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA Report No. 450/5-83-010b. pp. 5-75 to 5-82. 1983.

### 4.3.3 Sewage Sludge Incineration

#### Process Description

The first step in the process of sewage sludge incineration is dewatering the sludge. Sludge is generally dewatered until it is about 15 to 30 percent solids, at which point it will burn without supplemental fuel. After dewatering, the sludge is sent to the incinerator for combustion. The two main types of sewage sludge incinerators (SSIs) currently in use are the multiple-hearth furnace (MHF) and the fluidized-bed combustor (FBC). Over 80 percent of the identified operating sludge incinerators are MHFs and about 15 percent are FBCs. The remaining combustors co-fire MSW with sludge (U.S. EPA, 1995).

Multiple Hearth Furnaces (MHFs)--A cross-sectional diagram of a typical MHF is shown in Figure 4.3.3-1. The basic MHF is a vertically oriented cylinder. The outer shell is constructed of steel and lined with refractory material and surrounds a series of horizontal refractory hearths. A hollow cast iron rotating shaft runs through the center of the hearths. Cooling air is introduced into the shaft, which extends above the hearths. Attached to the central shaft are the rabble arms, which extend above the hearths. Each rabble arm is equipped with a number of teeth, approximately 6 inches in length and spaced about 10 inches apart. The teeth are shaped to rake the sludge in a spiral motion, alternating in direction from the outside in to the inside out between hearths. Burners, which provide auxiliary heat, are located in the sidewalls of the hearths.

In most MHFs, partially dewatered sludge is fed onto the perimeter of the top hearth. The rabble arms move the sludge through the incinerator by raking the sludge toward the center shaft, where it drops through holes located at the center of the hearth. In the next hearth, the sludge is raked in the opposite direction. This process is repeated in all of the subsequent hearths. The effect of the rabble motion is to break up solid material to allow better surface contact with heat and oxygen. A sludge depth of about 1 inch is maintained in each hearth at the design sludge flow rate.

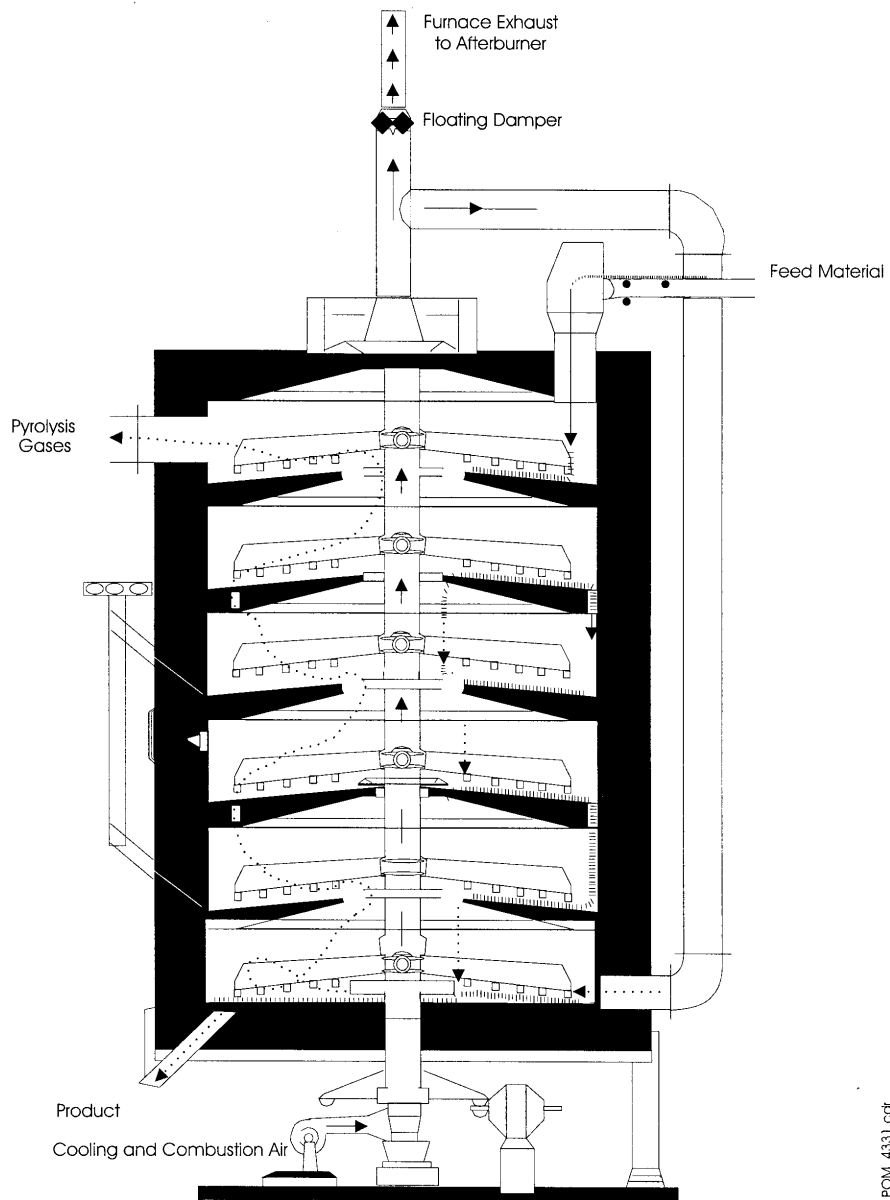


Figure 4.3.3-1. Typical Multiple-Hearth Furnace

Source: U.S. EPA, 1995.

Under normal operating conditions, 50 to 100 percent excess air must be added to an MHF in order to ensure complete combustion of the sludge. Besides enhancing contact between fuel and oxygen in the furnace, these relatively high rates of excess air are necessary to compensate for normal variations in both the organic characteristics of the sludge feed and the rate at which it enters the incinerator. When an inadequate amount of excess air is available, only partial oxidation of the carbon will occur, with a resultant increase in emissions of CO, soot, and hydrocarbons. Too much excess air, on the other hand, can cause increased entrainment of particulate and unnecessarily high auxiliary fuel consumption.

Fluidized-Bed Combustors--Figure 4.3.3-2 shows the cross-section diagram of an FBC.

Fluidized-bed combustors consist of a vertically oriented outer shell constructed of steel and lined with refractory material. Tuyeres (nozzles designed to deliver blasts of air) are located at the base of the furnace within a refractory-lined grid. A bed of sand, approximately 2.5 feet (0.75 meters) thick, rests upon the grid. Two general configurations can be distinguished on the basis of how the fluidizing air is injected into the furnace. In the hot windbox design, the combustion air is first preheated by passing it through a heat exchanger, where heat is recovered from the hot flue gases. Alternatively, ambient air can be injected directly into the furnace from a cold windbox.

Partially dewatered sludge is fed into the lower portion of the furnace. Air injected through the tuyeres at a pressure of 3 to 5 pounds per square inch gauge (20 to 35 kilopascals) simultaneously fluidizes the bed of hot sand and the incoming sludge. Temperatures of 1,400 to 1,700°F (750 to 925°C) are maintained in the bed. As the sludge burns, fine ash particles are carried out the top of the furnace. Some sand is also removed in the air stream and must be replaced at regular intervals.

Combustion of the sludge occurs in two zones. Within the sand bed itself (the first zone), evaporation of the water and pyrolysis of the organic materials occur nearly simultaneously as the temperature of the sludge is rapidly raised. In the freeboard area (the second zone), the remaining free carbon and combustible gases are burned. The second zone functions essentially as an afterburner.

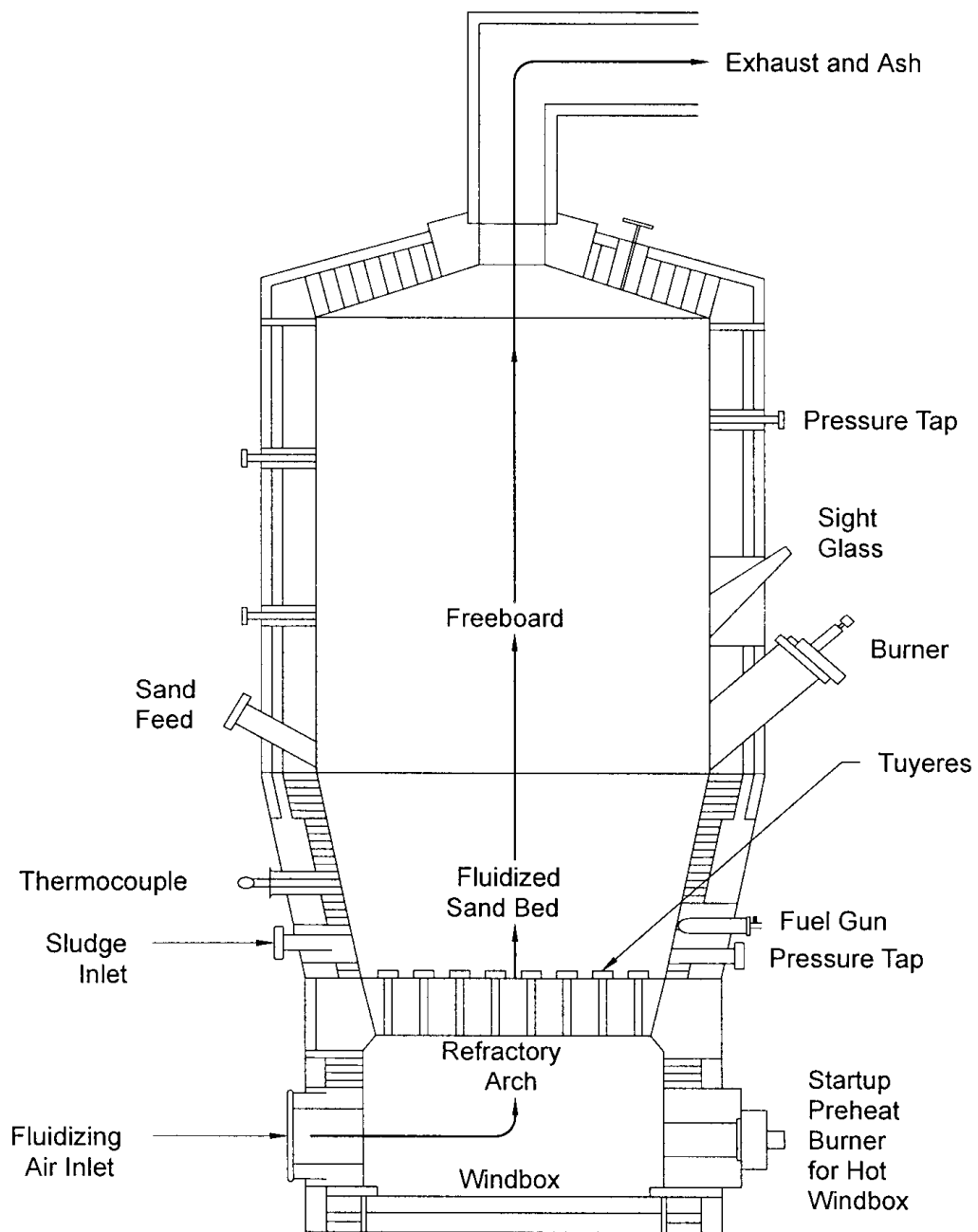


Figure 4.3.3-2. Fluidized-Bed Combustor

Source: U.S. EPA, 1995.

Fluidization achieves nearly ideal mixing between the sludge and the combustion air, and the turbulence facilitates the transfer of heat from the hot sand to the sludge. The most noticeable impact of the better burning atmosphere provided by an FBC is seen in the limited amount of excess air required for complete combustion of the sludge. Typically, FBCs can achieve complete combustion with 20 to 50 percent excess air, about half the excess air required by MHFs. As a consequence, FBCs have generally lower fuel requirements compared to MHFs.

Emission Control Techniques--Many SSIs have greater variability in their organic emissions than do other waste incinerators because, on average, sewage sludge has a high moisture content and that moisture content can vary widely during operation. Failure to achieve complete combustion of organic materials that evolve from the waste can result in emissions of a variety of organic compounds, including POM. In general, adequate oxygen, temperature, residence time, and turbulence will minimize emissions of most organics. The conditions of good combustion practices (GCP) are summarized as follows: (U.S. EPA, 1995)

- Uniform wastefeed;
- Adequate supply and good air distribution in the incinerator;
- Sufficiently high incinerator gas temperatures ( $1 >500^{\circ}\text{F}$  [ $>815^{\circ}\text{C}$ ]);
- Good mixing of combustion gas and air in all zones;
- Minimization of PM entrainment into the flue gas leaving the incinerator; and
- Temperature control of the gas entering the APCD to  $450^{\circ}\text{F}$  ( $230^{\circ}\text{C}$ ) or less.

Additional reductions in POM emissions may be achieved by utilizing PM control devices. The types of existing SSI PM controls range from low-pressure-drop spray towers and wet cyclones to higher-pressure-drop venturi scrubbers and venturi/impingement tray scrubber combinations. A few electrostatic precipitators and baghouses are employed, primarily where sludge is co-fired with MSW. The most widely used PM control device applied to an MHF is the



impingement tray scrubber. Older units use the tray scrubber alone; combination venturi/impingement tray scrubbers are widely applied to newer MHFs and some FBCs.

Afterburners may be utilized to achieve additional reduction of organic emissions in MHFs. Utilization of an afterburner provides a second opportunity for unburned hydrocarbons to be fully combusted. In afterburning, furnace exhaust gases are ducted to a chamber, where they are mixed with supplemental fuel and air and completely combusted. Additionally, some incinerators have the flexibility to allow sludge to be fed to a lower hearth, thus allowing the upper hearth(s) to function essentially as an afterburner.

### Emission Factors

The potential exists for many organic compounds to be emitted from SSIs because of the wide variety of organic compounds in the sludge. Lower molecular weight, volatile PAH compounds such as naphthalene may be emitted by volatilization of the compound. Higher weight PAH compounds can result from incomplete combustion of the sludge.

Naphthalene is the most commonly reported PAH from emissions testing at SSIs. One test study identified naphthalene as having one of the highest concentrations among semi-volatile compounds in pre-control flue gas. Test data associated with other PAHs are scarce, but the available data do show some PAH compounds besides naphthalene to be present in small quantities.

Table 4.3.3-1 provides PAH emission factors for SSIs. The factors presented cover the two main incinerator types: MHFs and FBCs. The factors for the MHF developed by Johnson et al. (1990) come from testing conducted at three SSIs in Ontario, Canada, and one in the United States. Naphthalene is by far the PAH compound emitted in the greatest quantity, and the FBC units showed the highest naphthalene emission factor among the different incinerator designs.

TABLE 4.3.3-1. PAH EMISSION FACTORS FOR SEWAGE SLUDGE INCINERATORS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
5-01-005-15	Multi-Hearth Furnace	Wet Scrubber	Benz(a)anthracene	1.24E-06 (0.62)	3.61E-08 - 2.40E-06 (0.02 - 1.2)	E	Johnson et al., 1990
			Benzo(a)pyrene	1.02E-06 (0.51)	5.21E-07 - 2.00E-06 (0.26 - 1)	E	Johnson et al., 1990
			Benzo(b)fluoranthene	1.40E-07 (0.07)	---	E	Johnson et al., 1990
			Benzo(k)fluoranthene	1.22E-06 (0.61)	1.04E-06 - 1.40E-06 (0.52 - 0.7)	E	Johnson et al., 1990
			Chrysene	1.44E-05 (7.20)	8.62E-06 - 1.98E-05 (4.30 - 9.9)	E	Johnson et al., 1990
			Indeno(1,2,3-cd)pyrene	2.00E-07 (0.10)	4.81E-08 - 3.61E-07 (0.02 - 0.18)	E	Johnson et al., 1990
			Acenaphthene	4.61E-07 (0.23)	4.41E-08 - 8.62E-07 (0.02 - 0.43)	E	Johnson et al., 1990
			Acenaphthylene	8.02E-09 (4.00E-03)	3.41E-09 - 1.38E-08 (0.00 - 0.0069)	E	Johnson, et al., 1990
			Anthracene	1.60E-07 (0.08)	2.81E-08 - 2.81E-07 (0.01 - 0.14)	E	Johnson et al., 1990
			Benzo(ghi)perylene	8.02E-08 (0.04)	1.6E-08 - 1.24E-07 (0.01 - 0.062)	E	Johnson et al., 1990
			Fluoranthene	1.24E-04 (62.00)	8.82E-06 - 3.81E-04 (4.40 - 190)	E	Johnson et al., 1990
Fluorene	8.82E-06 (4.40)	2.81E-06 - 1.80E-05 (1.40 - 9)	E	Johnson et al., 1990			

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(continued)

TABLE 4.3.3-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
5-01-005-15 (continued)	Multi-Hearth Furnace (continued)	Wet Scrubber (continued)	Naphthalene	3.20E-03 (1,597)	---	E	Gerstle, 1988
			Phenanthrene	8.82E-05 (44.00)	3.93E-05 - 1.80E-04 (19.60 - 90)	E	Johnson et al., 1990
			Pyrene	3.61E-06 (1.80)	3.21E-07 - 6.87E-06 (0.16 - 3.43)	E	Johnson et al., 1990
			Benzo(a)fluorene	1.76E-06 (0.88)	6.21E-07 - 2.81E-06 (0.31 - 1.4)	E	Johnson et al., 1990
			Benzo(e)pyrene	9.42E-07 (0.47)	4.41E-07 - 1.44E-06 (0.22 - 0.72)	E	Johnson et al., 1990
			Coronene	8.02E-08 (0.04)	ND - 1.48E-07 (ND - 0.074)	E	Johnson et al., 1990
			Methylanthracenes	1.80E-07 (0.09)	8.02E-09 - 3.41E-07 (0.00 - 0.17)	E	Johnson et al., 1990
			Methylphenanthrenes	7.82E-06 (3.90)	6.49E-05 - 9.02E-06 (32.40 - 4.5)	E	Johnson et al., 1990
			Perylene	6.01E-08 (0.03)	6.01E-09 - 1.34E-07 (0.00 - 0.067)	E	Johnson et al., 1990
5-01-005-15	Multi-Hearth Furnace	Cyclone/ Venturi	Naphthalene	1.94E-03 (970.00)	---	D	U.S. EPA, 1995
5-01-005-15	Multi-Hearth Furnace	None	Naphthalene	1.84E-02 (9,200.00)	---	E	U.S. EPA, 1995
5-01-005-15	Fluidized-Bed Combustor	Venturi/ Impingement	Naphthalene	1.94E-01 (97,000.00)	---	E	U.S. EPA, 1995

<sup>a</sup>Emission factors are expressed in lb (mg) pollutant emitted per ton (Mg) of dry sludge incinerated.

“--” means data not available.

## Source Location

There are approximately 170 sewage sludge incineration plants in operation in the United States. Most sludge incinerators are located in the eastern United States, though there are a significant number on the West Coast. New York has the largest number of facilities with 33. Pennsylvania and Michigan have the next largest number of facilities with 21 and 19 sites, respectively (U.S. EPA, 1990).

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U.S. Environmental Protection Agency. Locating and Estimating Air Toxics Emissions from Sewage Sludge Incinerators. Office of Air Quality Standards, Research Triangle Park, North Carolina. EPA-450/2-90-009. May 1990.

#### 4.3.4 Medical Waste Incineration

Medical waste incinerators (MWIs) burn wastes produced by hospitals, veterinary facilities, crematories, and medical research facilities. These wastes include both infectious (“red bag” and pathological) medical wastes and non-infectious general hospital wastes. The primary purposes of MWIs are to (1) render the waste innocuous, (2) reduce the volume and mass of the waste, and (3) provide waste-to-energy conversion. The total population of MWIs is estimated at 5,000, with the following distribution by facility category: 3,150 MWIs or 63 percent at hospitals, 500 MWIs or 10 percent at laboratories, 550 MWIs or 11.6 percent at veterinary facilities, 500 MWIs or 10 percent at nursing homes, and 300 MWIs at commercial and other unidentified facilities (U.S. EPA, 1994).

##### Process Description

Three main types of incinerators are used as MWIs: controlled-air or starved-air, excess-air, and rotary kiln. The majority (>95 percent) of incinerators are controlled-air units. A small percentage (<2 percent) are excess-air, and less than 1 percent were identified as rotary kiln. The rotary kiln units tend to be larger, and typically are equipped with air pollution control devices. Approximately 2 percent of all the incinerators identified were equipped with air pollution control devices (U.S. EPA, 1995).

Controlled-Air Incinerators--As noted above, controlled-air incineration is the most widely used MWI technology, and now dominates the market for new systems at hospitals and similar medical facilities. This technology is also known as two-stage incineration or modular combustion. Figure 4.3.4-1 presents a schematic diagram of a typical controlled-air unit.

Combustion of waste in controlled-air incinerators occurs in two stages. In the first stage, waste is fed into the primary, or lower, combustion chamber, which is operated with less than the stoichiometric amount of air required for combustion. Combustion air enters the primary chamber from beneath the incinerator hearth (below the burning bed of waste). This air is called primary or underfire air. In the primary (starved-air) chamber, the low air-to-fuel ratio

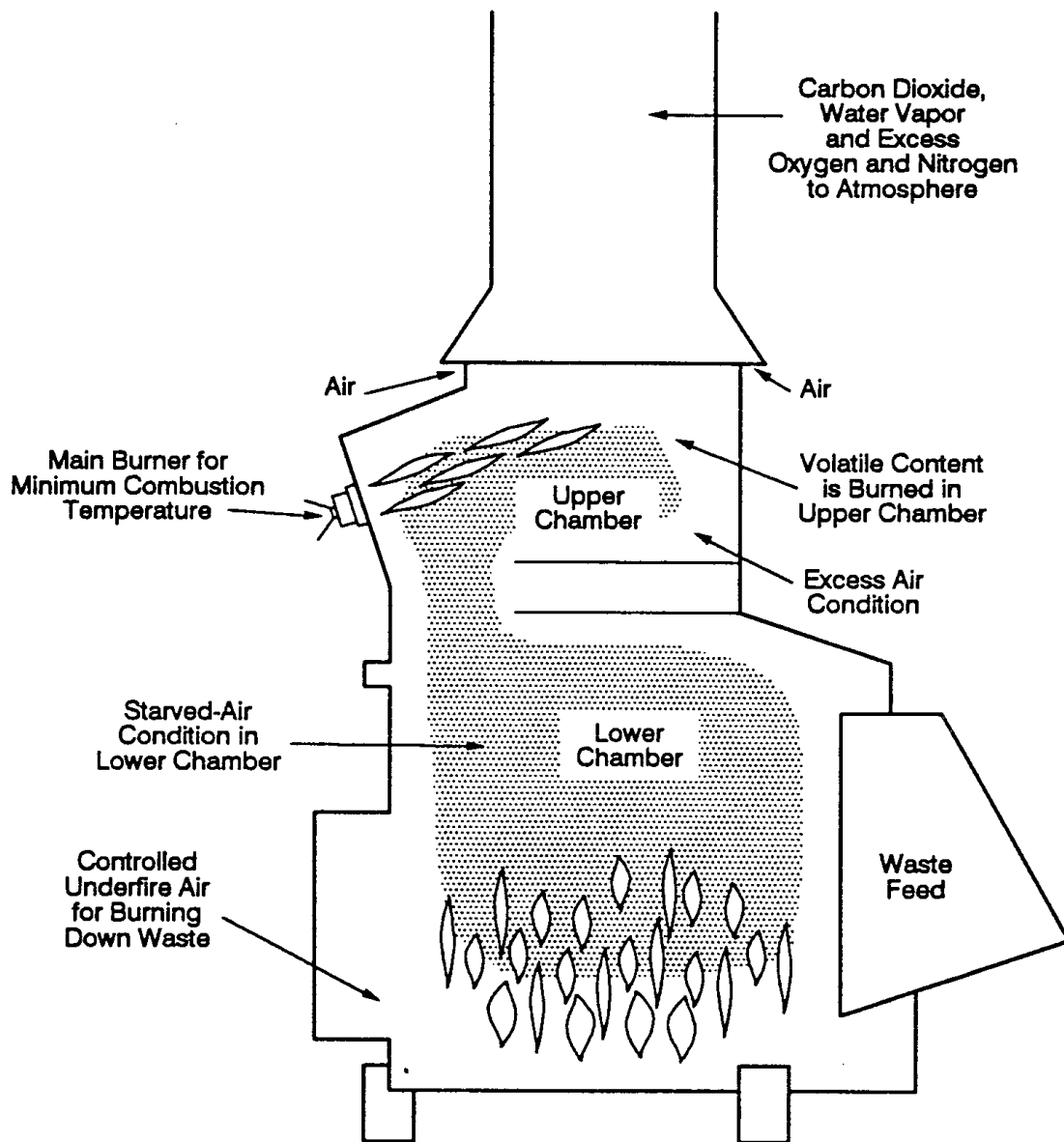


Figure 4.3.4-1. Controlled-Air Incinerator

Source: U.S. EPA, 1995.

dries and facilitates volatilization of the waste and most of the residual carbon in the ash burns. At these conditions, combustion gas temperatures are relatively low (1,400 to 1,800°F [760 to 980°C]).

In the second stage, excess air is added to the volatile gases formed in the primary chamber to complete combustion. Secondary chamber temperatures are higher than primary chamber temperatures--typically 1,800 to 2,000°F (980 to 1,095°C). Depending on the heating value and moisture content of the waste, additional heat may be needed. This can be provided by auxiliary burners located at the entrance to the secondary (upper) chamber to maintain desired temperatures.

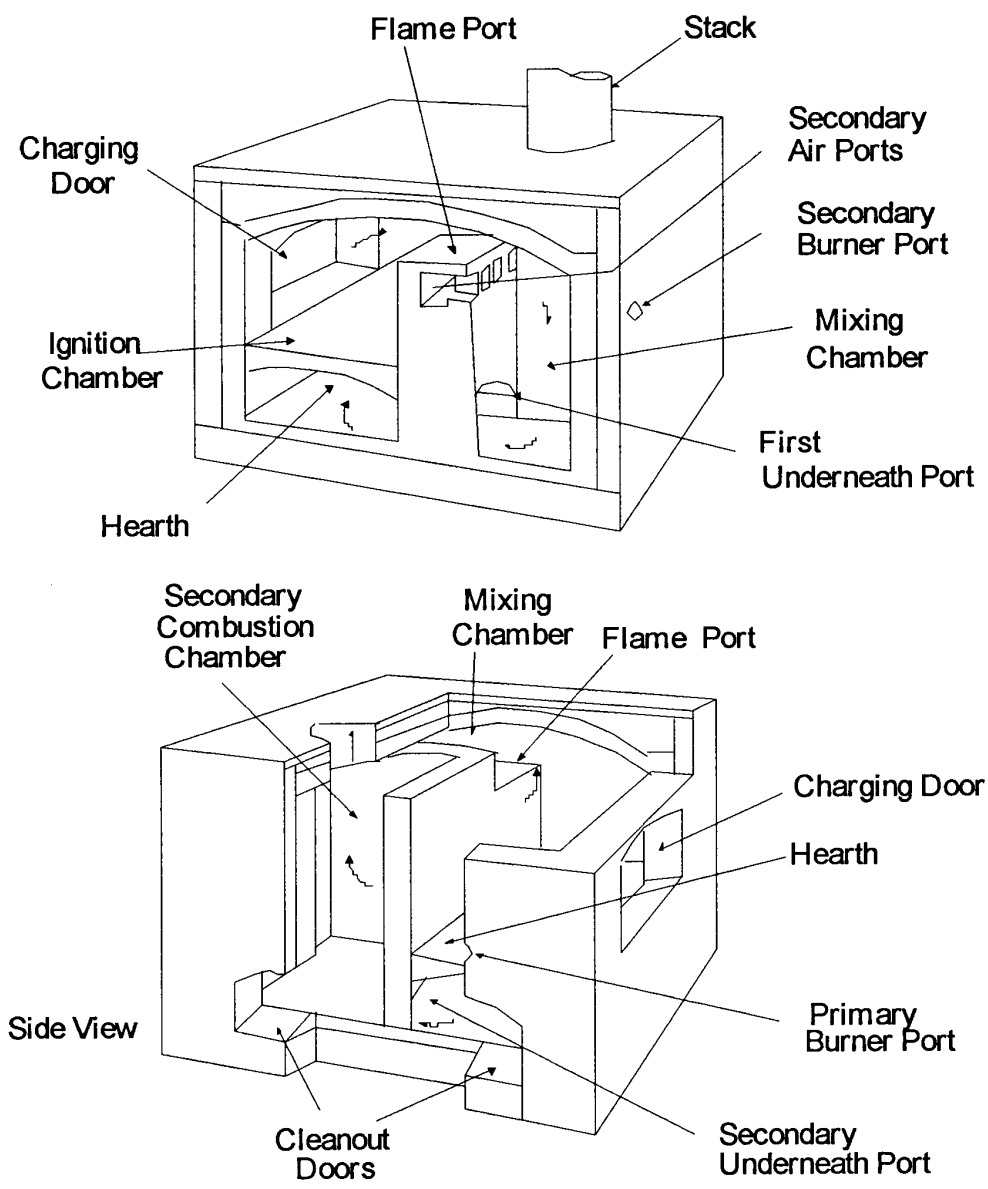
Waste feed capacities for controlled-air incinerators range from about 75 to 6,500 lb/hr (0.6 to 50 kg/min) (at an assumed fuel heating value of 8,500 Btu/lb [19,700 kJ/kg]). Waste feed and ash removal can be manual or automatic, depending on the unit size and options purchased. Throughput capacities for lower-heating-value wastes may be higher because feed capacities are limited by primary chamber heat release rates. Heat release rates for controlled-air incinerators typically range from about 15,000 to 25,000 Btu/hr-ft<sup>3</sup> (430,000 to 710,000 KJ/hr-m<sup>3</sup>).

Excess-Air Incinerators--Excess-air incinerators are typically small modular units. They are also referred to as batch incinerators, multiple-chamber incinerators, or “retort” incinerators.

Excess-air incinerators are typically a compact cube with a series of internal chambers and baffles. Although they can be operated continuously, they are usually operated in a batch mode.

Figure 4.3.4-2 presents a schematic for an excess-air unit. Typically, waste is manually fed into the combustion chamber. The charging door is then closed and an afterburner is ignited to bring the secondary chamber to a target temperature (typically 1,600 to 1,800°F [870 to 980°C]). When the target temperature is reached, the primary chamber burner ignites. The waste is dried, ignited, and combusted by heat provided by the primary chamber burner, as well as by radiant heat from the chamber walls. Moisture and volatile components in the waste are vaporized and pass (along with combustion gases) out of the primary chamber and through a





ERG\_Lead\_513.cdr

Figure 4.3.4-2. Excess-Air Incinerator

Source: U.S. EPA, 1995.

flame port that connects the primary chamber to the secondary or mixing chamber. Secondary air is added through the flame port and is mixed with the volatile components in the secondary chamber. Burners are also installed in the secondary chamber to maintain adequate temperatures for combustion of volatile gases. Gases exiting the secondary chamber are directed to the incinerator stack or to an air pollution control device. After the chamber cools, ash is manually removed from the primary chamber floor and a new charge of waste can be added.

Incinerators designed to burn general hospital waste operate at excess air levels of up to 300 percent. If only pathological wastes are combusted, excess air levels near 100 percent are more common. The lower excess air helps maintain higher chamber temperature when burning high-moisture waste. Waste feed capacities for excess-air incinerators are usually 500 lb/hr (3.8 kg/min) or less.

Rotary Kiln Incinerators--Rotary kiln incinerators, like the other types, are designed with a primary chamber, where the waste is heated and volatilized, and a secondary chamber, where combustion of the volatile fraction is completed. The primary chamber consists of a slightly inclined, rotating kiln in which waste materials migrate from the feed end to the ash discharge end. The waste throughput rate is controlled by adjusting the rate of kiln rotation and the angle of inclination. Combustion air enters the primary chamber through a port. An auxiliary burner is generally used to start combustion and maintain desired combustion temperatures.

Figure 4.3.4-3 presents a schematic diagram of a typical rotary kiln incinerator. Volatiles and combustion gases pass from the primary chamber to the secondary chamber. The secondary chamber operates at excess air. Combustion of the volatiles is completed in the secondary chamber. Because of the turbulent motion of the waste in the primary chamber, solids burnout rates and particulate entrainment in the flue gas are higher for rotary kiln incinerators than for other incinerator designs. As a result, rotary kiln incinerators generally have add-on gas-cleaning devices.

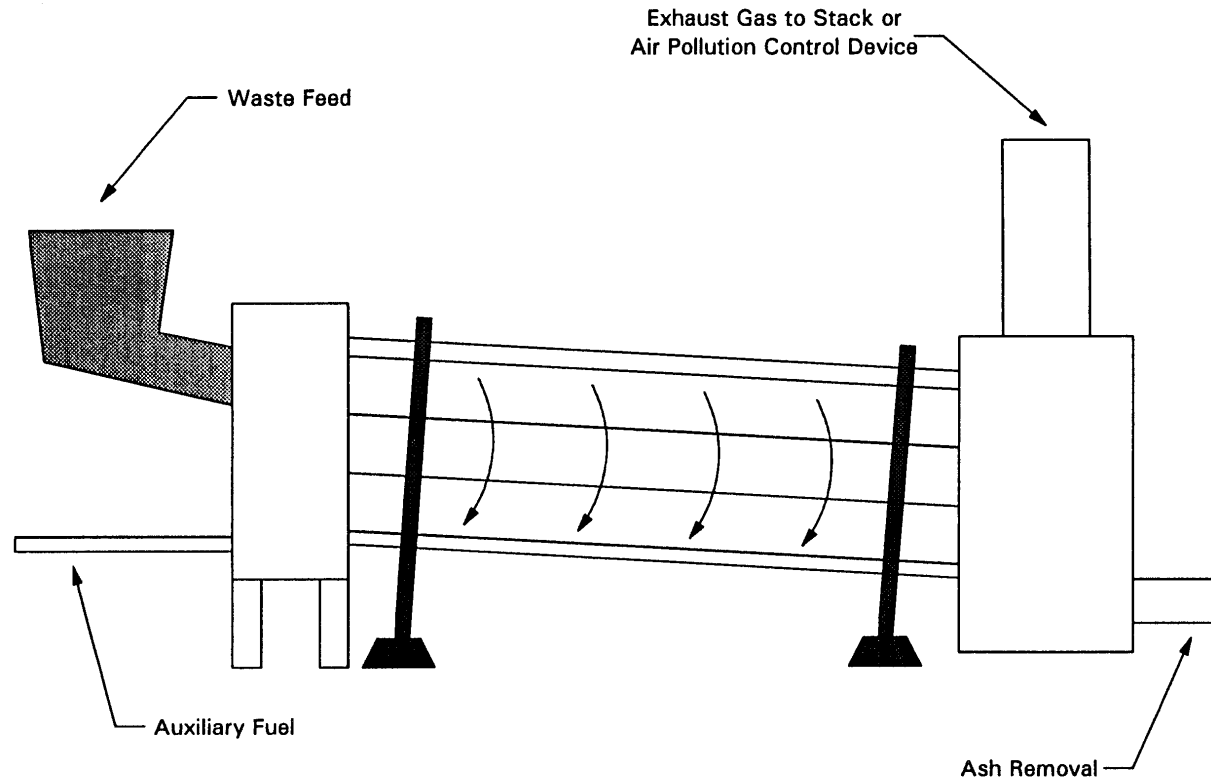


Figure 4.3.4-3. Rotary Kiln Incinerator

Source: U.S. EPA, 1995.

Emission Control Techniques--Air emissions of organic compounds from MWIs are controlled primarily by promoting complete combustion through the use of Good Combustion Practice (GCP). As noted above, only a small percentage of MWIs use air pollution control devices. The most frequently used devices are wet scrubbers and fabric filters. Fabric filters mainly provide PM control. Other PM control technologies include venturi scrubbers and electrostatic precipitators (ESPs). Generally, any of the PM control technologies will have a beneficial effect in reducing particulate-phase PAH emissions as well.

Emissions of PAHs from MWIs are suspected to result primarily from incomplete combustion. In general, GCP conditions such as adequate oxygen, temperature, residence time, and turbulence will minimize emissions of most organics. There are little test data to support any firm conclusions, but it is likely that advanced incinerators operating under GCPs will have lower emissions of PAHs than poorly maintained or poorly operated incinerators. There are many small MWIs that are not operating at maximum efficiency because of the minimal amount of operator control over these units; these units would be expected to emit higher amounts of PAHs.

#### Emission Factors

The available PAH emission factors for MWIs are presented in Table 4.3.4-1. Data for PAHs other than naphthalene were not available. It is expected that other PAHs are also emitted as part of the combustion process and, as with MWCs, waste composition is a critical factor in the amount of PAHs emitted.

The naphthalene factors developed by Walker and Cooper (1992), are based on the operating test data from 17 MWIs. Data from 11 MWI facilities with emission controls and 6 MWI facilities without controls were analyzed. The facilities tested burned red bag waste, pathological waste, and/or general hospital waste. For this study, red bag waste was defined as any waste generated in the diagnosis or immunization of human beings or animals; pathological waste was defined as any human and animal remains, tissues, and cultures; and general hospital waste was defined as a mixture of red bag waste and municipal waste generated by the hospital.

TABLE 4.3.4-1. PAH EMISSION FACTORS FOR MEDICAL WASTE INCINERATORS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating
5-01-005-05	Medical Waste Incinerators, Multi-Chamber and Single-Chamber	None	Naphthalene	1.62E-03 (808)	1.93E-04 - 1.26E-02 (96.4 - 6,300)	C
5-01-005-05	Medical Waste Incinerators, Multi-Chamber and Single-Chamber	Scrubber/Baghouse	Naphthalene	2.24E-04 (112)	1.56E-04 - 2.95E-04 (77.8 - 147)	C

<sup>a</sup>Emission factors are expressed as lb (mg) of naphthalene emitted per ton (Mg) of medical waste incinerated.

Source: Walker and Cooper, 1992.

## Source Location

There are an estimated 5,000 MWIs in the United States, located at such facilities as hospitals, pharmaceutical companies, research facilities, nursing homes, and other institutions and companies that incinerate medical waste (U.S EPA, 1993).

#### SECTION 4.3.4 REFERENCES

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#### 4.3.5 Hazardous Waste Incineration

Hazardous waste, as defined by the Resource Conservation and Recovery Act (RCRA) in 40 CFR Part 261, includes a wide variety of waste materials. Hazardous wastes are produced in the form of liquids (e.g., waste oils, halogenated and nonhalogenated solvents, other organic liquids, and pesticides/herbicides) and sludges and solids (e.g., halogenated and nonhalogenated sludges and solids, dye and paint sludges, resins, and latex). Based on a 1986 study, total annual hazardous waste generation in the United States was approximately 292 million tons (265 million metric tons) (Oppelt, 1987). Only a small fraction of the waste (<1 percent) was incinerated.

Based on an EPA study conducted in 1983, the major types of hazardous waste streams incinerated were spent nonhalogenated solvents and corrosive and reactive wastes contaminated with organics. Together, these accounted for 44 percent of the waste incinerated. Other prominent wastes included hydrocyanic acid, acrylonitrile bottoms, and nonlisted ignitable wastes.

Industrial kilns, boilers, and furnaces also burn hazardous wastes as fuel to produce commercially viable products such as cement, lime, iron, asphalt, or steam. These industrial sources require large inputs of fuel to produce the desired product. Hazardous waste, which is considered an economical alternative to fossil fuels for energy and heat, is utilized as a supplemental fuel. In the process of producing energy and heat, the hazardous wastes are subjected to high temperatures for a sufficient time to destroy the hazardous content and the bulk of the waste. The sections of this document describing Portland Cement Kilns, the Pulp and Paper Industry, and Waste Oil Incineration include discussions of POM emissions from these sources.

#### Process Description

Hazardous waste incineration is a process that employs thermal decomposition via thermal oxidation at high temperatures (usually 1,650°F [900°C] or greater) to destroy the



organic fraction of the waste and reduce volume. A diagram of the typical process component options in a hazardous waste incineration facility is provided in Figure 4.3.5-1. The diagram shows the major subsystems that may be incorporated into a hazardous waste incineration system: (1) waste preparation and feeding, (2) combustion chamber(s), (3) air pollution control, and (4) residue/ash handling.

Five types of hazardous waste incinerators are currently available and in operation: liquid injection, rotary kiln, fixed-hearth, fluidized-bed, and fume injection (U.S. EPA, 1986). Additionally, a few other technologies have been used for incineration of hazardous waste, including ocean incineration vessels and mobile incinerators. These processes are not in widespread use in the United States and are not discussed below.

Liquid Injection Incinerators--Liquid injection combustion chambers are applicable almost exclusively for pumpable liquid waste, including some low-viscosity sludges and slurries. Liquid injection units are usually simple, refractory-lined cylinders (either horizontally or vertically aligned) equipped with one or more waste burners. The typical capacity of liquid injection units is about 8 to 28 million Btu/hour (8.4 to 29.5 GJ/hour). Figure 4.3.5-2 presents a schematic diagram of a typical liquid injection unit (U.S. EPA, 1986; Oppelt, 1987).

Rotary Kiln Incinerators--Rotary kiln incinerators are used in the destruction of solid wastes, slurries, containerized waste, and liquids. Because of their versatility, these types of units are most frequently used by commercial off-site incineration facilities. Rotary kiln incinerators generally consist of two combustion chambers: a rotating kiln and an afterburner. The rotary kiln is a cylindrical refractory-lined shell that is mounted on a slight incline. The primary function of the kiln is to convert solid wastes to gases, which occurs through a series of volatilization, destructive distillation, and partial combustion reactions. The typical capacity of these units is about 10 to 60 million Btu/hour (10.5 to 63.3 GJ/hour). Figure 4.3.5-3 presents a schematic diagram of a typical rotary kiln unit.

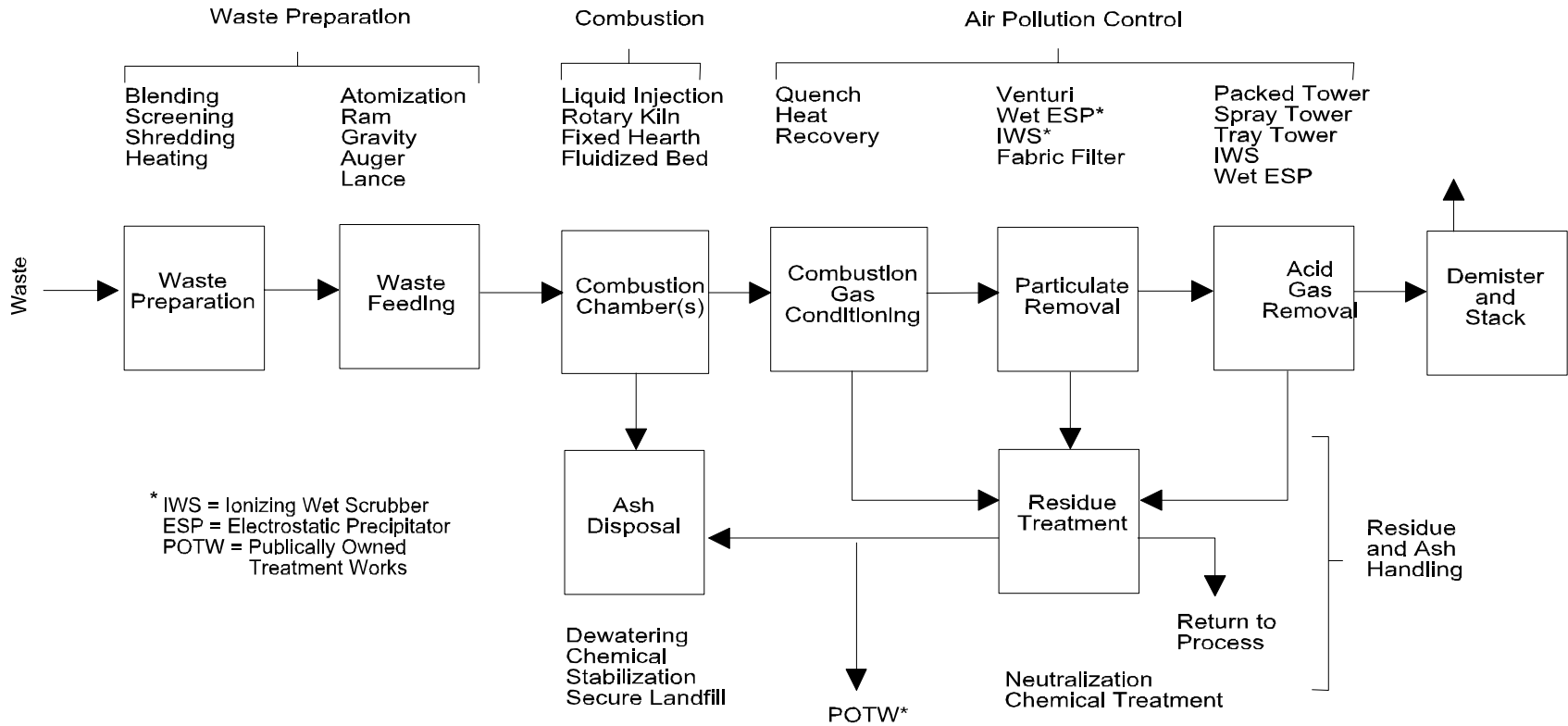


Figure 4.3.5-1. Typical Process Component Options in a Hazardous Waste Incineration Facility

Source: Oppelt, 1987.

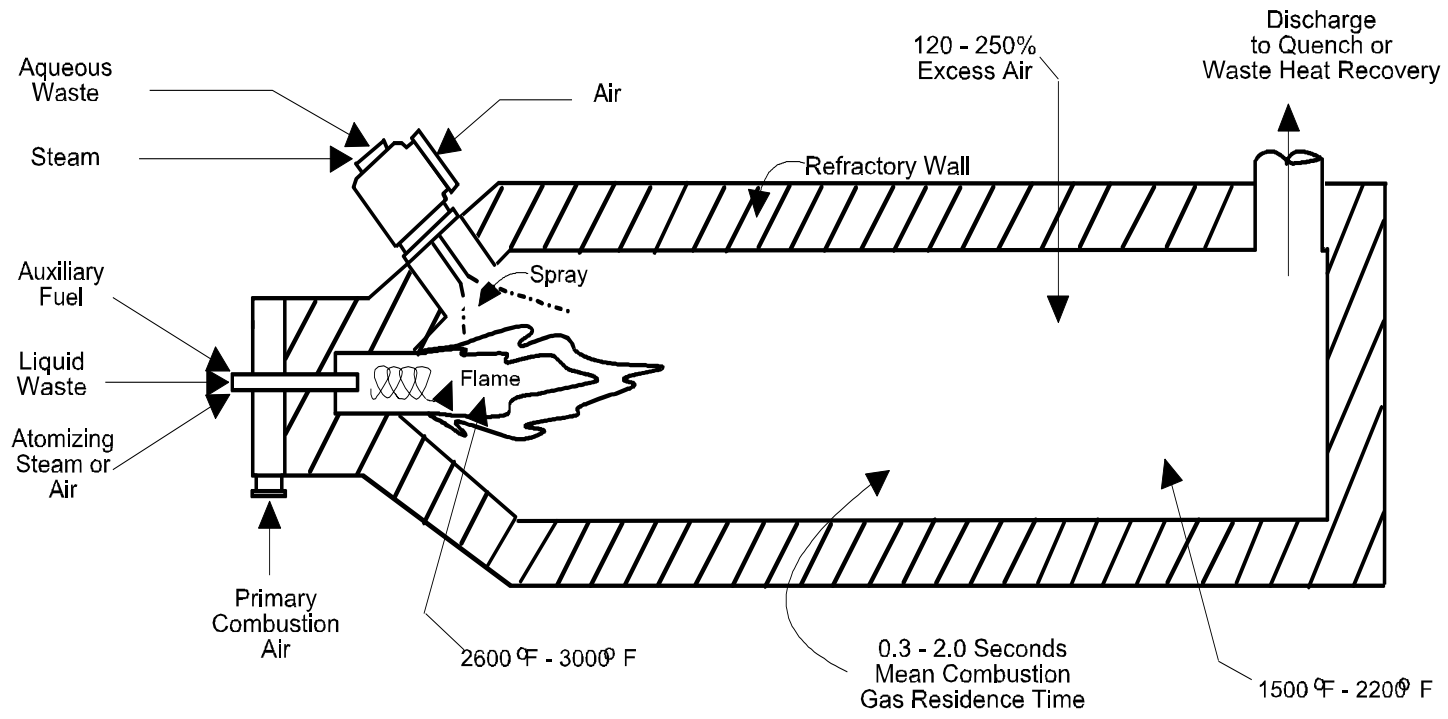


Figure 4.3.5-2. Typical Liquid Injection Combustion Chamber

Source: Oppelt, 1987.

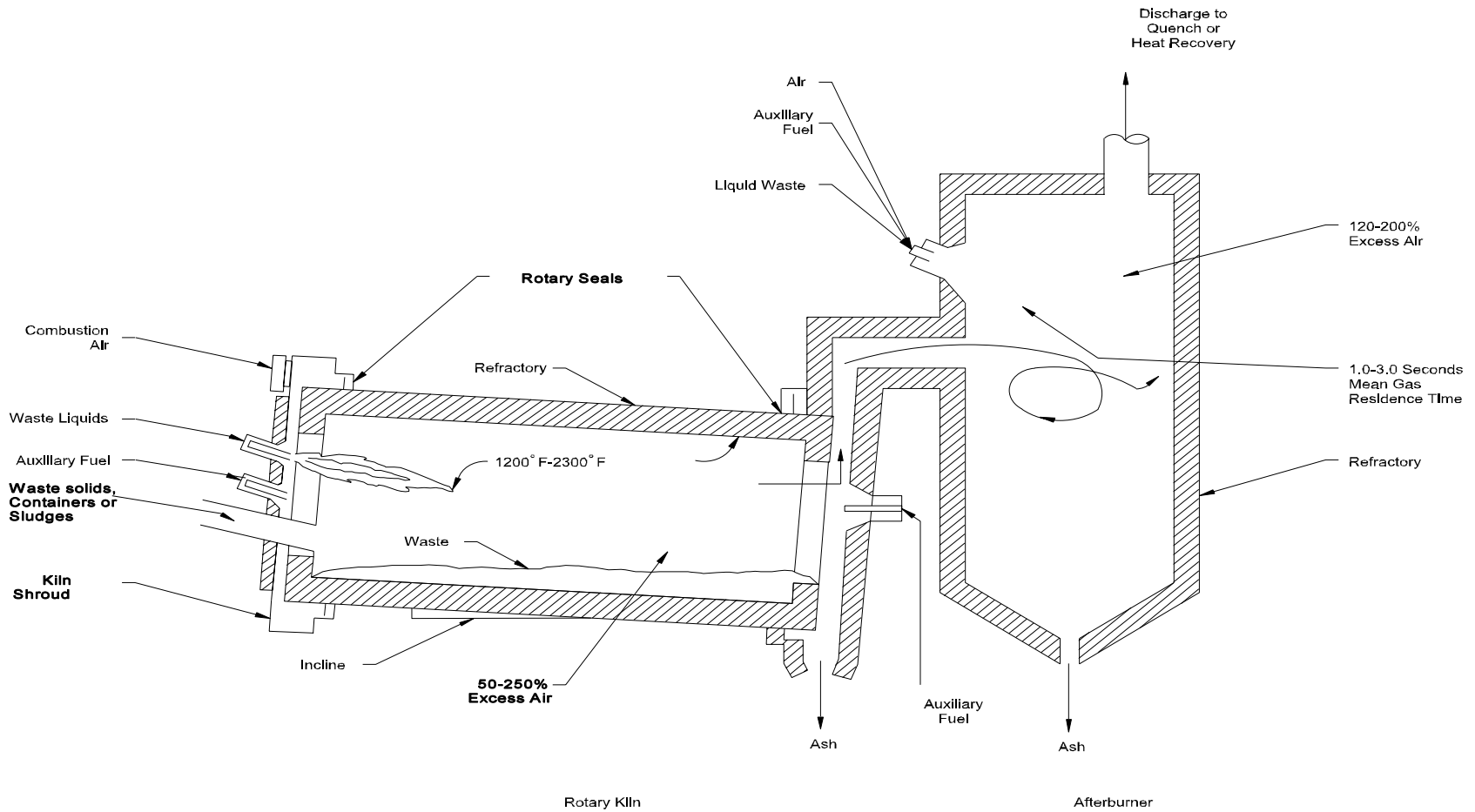


Figure 4.3.5-3. Typical Rotary Kiln/Afterburner Combustion Chamber

Source: Oppelt, 1987.

An afterburner is connected directly to the discharge end of the kiln. The afterburner is used to ensure complete combustion of flue gases before their treatment for air pollutants. A tertiary combustion chamber may be added if needed. The afterburner itself may be horizontally or vertically aligned, and functions on much the same principles as the liquid injection unit described above. Both the afterburner and the kiln are usually equipped with an auxiliary fuel-firing system to control the operating temperature.

Fixed-hearth Incinerators--Figure 4.3.5-4 presents a schematic diagram of a typical fixed-hearth unit (U.S EPA, 1986; Oppelt, 1987). Fixed-hearth incinerators, also called controlled-air, starved-air, or pyrolytic incinerators, are the third major technology used for hazardous waste incineration (Oppelt, 1987). This type of incinerator may be used for the destruction of solid, sludge, and liquid wastes. Fixed-hearth units tend to be of smaller capacity (typically 5 million Btu/hour [5.3 GJ/hour]) than liquid injection or rotary kiln incinerators because of physical limitations in ram feeding and transporting large amounts of waste materials through the combustion chamber.

Fixed-hearth units consist of a two-stage combustion process, similar to that of rotary kilns. Waste is ram fed into the primary chamber and burned at about 50 to 80 percent of stoichiometric air requirements. This starved-air condition causes most of the volatile fraction to be destroyed pyrolytically. The resultant smoke and pyrolytic products pass to the secondary chamber, where additional air and, in some cases, supplemental fuel, is injected to complete the combustion (Oppelt, 1987).

Fluidized-bed Incinerators--Fluidized-bed incinerators, described in Section 4.3.3 of this report, have only recently been applied to hazardous waste incineration. FBCs used to dispose of hazardous waste are very similar to those used to incinerate sewage sludge except for their additional capability of handling liquid wastes.

FBCs are suitable for disposing of combustible solids, liquids, and gaseous wastes. They are not suited for irregular, bulky wastes, tarry solids, or other wastes that leave residues in the bed (Whitworth, 1992). Fluidized bed combustion chambers consist of a single

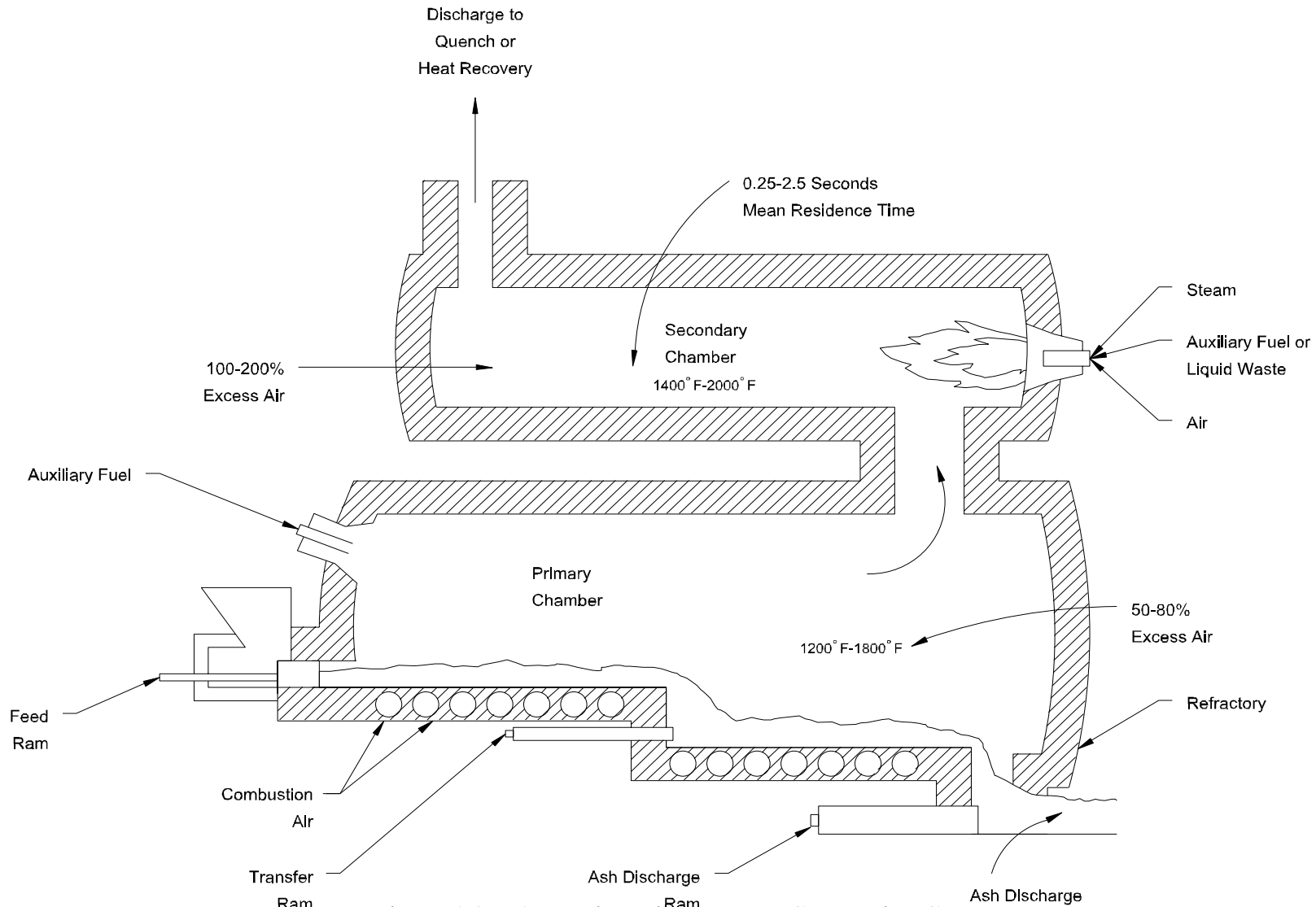


Figure 4.3.5-4. Typical Fixed-Hearth Combustion Chamber

Source: Oppelt, 1987.

refractory-lined combustion vessel partially filled with inert granular material (e.g., particles of sand, alumina, and sodium carbonate) (Oppelt, 1987). The typical capacity of this type of incinerator is 45 million Btu/hour (47.5 GJ/hour).

Fume Injection Incinerators--Fume injection incinerators are used exclusively to destroy gaseous or fume wastes. The combustion chamber is comparable to that of a liquid-injection incinerator (Figure 4.3.5-2) in that it usually has a single chamber, is vertically or horizontally aligned, and uses nozzles to inject the waste into the chamber for combustion. Waste gases are injected by pressure or atomization through the burner nozzles. Wastes may be combusted solely by thermal or catalytic oxidation.

Emission Control Techniques--Most organics control for hazardous waste incinerators is achieved by promoting complete combustion through GCP. The conditions of GCP are summarized in Section 4.3.3, Sewage Sludge Incineration. Failure to achieve complete combustion of organic materials evolved from the waste can result in emissions of a variety of organic compounds, including POM. In general, adequate oxygen, temperature, residence time, and turbulence will minimize emissions of most organics.

Additionally, control of organics, including POM, may be partially achieved by using PM control devices. The most frequently used control devices for PM control are wet scrubbers and fabric filters. Other PM control technologies include venturi scrubbers and electrostatic precipitators (ESPs).

#### Emission Factors

Few test data are available on POM emissions from hazardous waste incinerators. The available data have primarily included only naphthalene emissions measurements. However, it is expected that, as with other combustion sources, other PAH compounds are emitted as a result of incomplete combustion and possibly from the fuel itself. The composition of the fuel, or waste in this case, varies tremendously in the hazardous waste incineration industry, more so than with most of the other combustion sources discussed in this document. In many cases, the

fuel represents a combination of many different wastes and, depending on the content, may or may not result in significant POM emissions.

PAH emission factors for hazardous waste incineration are provided in Table 4.3.5-1. These factors represent the incineration of various types of hazardous wastes in different combustion configurations. Because of the impact of waste composition on PAH emissions, these factors should be used only as a relative measure of PAH emissions from hazardous waste incinerators. The characterization of each of the individual waste types that were incinerated at the facilities on which these factors are based were not available; therefore, it is impossible to assume that these factors are applicable to any given hazardous waste incinerator scenario. It should be noted, however, that naphthalene can be one of the more important PAHs emitted from this source in terms of quantity of emissions. Another test study of various hazardous waste incinerators, including liquid injection, rotary kiln and hearth configurations, reported concentrations of naphthalene in the exhaust gas that were 100 times greater than the two other reported compounds, pyrene and fluoranthene (Trenholm et al., 1984). The high concentrations reported for naphthalene relative to other PAHs is consistent with other waste combustion source categories covered earlier in this document.

#### Source Location

Approximately 221 hazardous waste incinerators are operating under the Resource Conservation and Recovery Act (RCRA) system in the United States. These incinerators are located at 189 separate facilities, 171 of which are located at the site of waste generation (Oppelt, 1987). Texas has the most incinerators with 27 facilities, followed by Louisiana and Ohio, each with 17 facilities, and California with 15 facilities. Some of the smaller incinerators and those that are designed to be mobile are not permanent facilities, but are set up at the site where the waste is being removed. Other facilities are permanent and accept waste from different sites across the country.



TABLE 4.3.5-1. PAH EMISSION FACTORS FOR HAZARDOUS WASTE INCINERATORS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
5-03-005-01	Liquid Injection Incinerator for Mixed Liquid Industrial Waste, Dual-Chamber Design	Scrubber/Baghouse	Benz(a)anthracene	6.01E-06 (3.00)	E	Johnson et al., 1990
			Benzo(a)pyrene	2.00E-06 (1.00)	E	Johnson et al., 1990
			Benzo(a)fluoranthene	5.01E-06 (2.50)	E	Johnson et al., 1990
			Chrysene/Triphenylene	1.10E-05 (5.50)	E	Johnson et al., 1990
			Dibenz(a,h)anthracene	1.20E-06 (0.60)	E	Johnson et al., 1990
			Indeno(1,2,3-cd)pyrene	3.81E-06 (1.90)	E	Johnson et al., 1990
			Acenaphthene	7.21E-06 (3.60)	E	Johnson et al., 1990
			Benzo(ghi)perylene	4.21E-06 (2.10)	E	Johnson et al., 1990
			Anthracene	1.16E-05 (5.80)	E	Johnson et al., 1990
			Fluoranthene	4.97E-05 (24.80)	E	Johnson et al., 1990
			Fluorene	1.34E-05 (6.70)	E	Johnson et al., 1990
Phenanthrene	1.01E-04 (50.20)	E	Johnson et al., 1990			

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(continued)

TABLE 4.3.5-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
5-03-005-01 (continued)	Liquid Injection Incinerator for Mixed Liquid Industrial Waste, Dual-Chamber Design (continued)	Scrubber/Baghouse (continued)	Pyrene	2.81E-05 (14.00)	E	Johnson et al., 1990
			Benzo(e)pyrene	2.00E-06 (1.00)	E	Johnson et al., 1990
			Coronene	2.61E-06 (1.30)	E	Johnson et al., 1990
			Methylanthracenes	3.79E-05 (18.90)	E	Johnson et al., 1990
			Methylphenanthrenes	1.76E-05 (8.80)	E	Johnson et al., 1990
			Perylene	6.01E-07 (0.30)	E	Johnson et al., 1990
			Acenaphthalene	5.41E-06 (2.70)	E	Johnson et al., 1990
5-03-005-01	Hazardous Waste Incinerator	Unknown	Naphthalene	102.586 lb/MMBtu (44.00 ng/kJ)	E	Oppelt, 1987
5-03-005-01	Industrial Boiler Burning Hazardous Waste	Unknown	Naphthalene	1.3989 lb/MMBtu (0.60 ng/kJ)	E	Oppelt, 1987

<sup>a</sup>Emission factors are expressed as lb (mg) of pollutant per ton (Mg) of waste incinerated, except where otherwise indicated.

#### SECTION 4.3.5 REFERENCES

Johnson, N.D., M.T. Scholtz, V. Cassaday, and K. Davidson. MOE Toxic Chemical Emission Inventory for Ontario and Eastern North America. Prepared for the Air Resources Branch, Ontario Ministry of the Environment, Rexdale, Ontario. Draft Report No. P.89-50-5429/OG. p. 151. 1990.

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Whitworth, W.E., L.E. Waterland. Pilot-Scale Incineration of PCB-Contaminated Sediments from the Hot Spot of the New Bedford Harbor Superfund Site. Acurex Corporation. Jefferson, Arkansas. 1992.

#### 4.3.6 Drum and Barrel Reclamation

##### Process Description

POM emissions have been detected in the stack gases from drum reclamation facilities. These facilities typically consist of a furnace that is used to heat the drums to an elevated temperature in order to destroy any residual materials in the containers. The drums are then repaired, repainted, relined, and sold for reuse.

The drums processed at these facilities come from a variety of sources, such as the petroleum and chemical industries, and sometimes contain residual waste that is classified as hazardous according to the EPA's Resource Conservation and Recovery Act (RCRA) guidelines.

The furnaces are fired by an auxiliary fuel such as oil or natural gas. The used drums are typically loaded onto a conveyor, which carries them through the heat treatment zone. As the drums proceed through this process, any residual contents, paint, and interior linings are burned off or disintegrated. POM formation can occur from either the heat treatment of the barrels or from the combustion of the auxiliary fuel.

##### Emission Factors

Only one test report (Galson Corporation, 1992) was found that measured emissions of specific PAH compounds from a drum reclamation facility. The facility tested recycles 55-gallon drums. There was no indication as to the physical or chemical characteristics of the residual waste in the drums, or of the auxiliary fuel type used to fire the furnace. The drum furnace consists of a boiler with a 10,200 Btu/hr capacity in conjunction with a 8,256,000 Btu/hr boiler and an afterburner that serves as an emissions control device. Table 4.3.6-1 shows PAH emission factors developed for this facility.

TABLE 4.3.6-1. PAH EMISSION FACTORS FOR DRUM AND BARREL RECLAMATION

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1000 barrels (mg/1000 barrels) <sup>a</sup>	Emission Factor Rating
5-03-005-01	55-gallon Drum Recycling Furnace	Afterburner	Benz(a)anthracene	3.54E-07 (0.16)	E
			Benzo(b)fluoranthene	1.33E-07 (0.06)	E
			Chrysene	6.63E-08 (0.03)	E
			Acenaphthene	2.85E-06 (1.29)	E
			Acenaphthylene	7.07E-07 (0.32)	E
			Anthracene	2.63E-06 (1.19)	E
			Fluoranthene	5.30E-07 (0.24)	E
			Fluorene <sup>b</sup>	6.32E-06 (2.86)	E
			Naphthalene <sup>b</sup>	1.67E-05 (7.54)	E
			Phenanthrene <sup>b</sup>	4.66E-06 (2.11)	E
			Pyrene	6.63E-07 (0.3)	E

<sup>a</sup>Emission factors are expressed in lb (mg) of pollutant emitted per thousand 55-gallon barrels processed.

<sup>b</sup>Compound also detected in field blank; emission rate not adjusted for field blank detection.

Source: Galson Corporation, 1992.

The emission factors for drum reclamation should be used cautiously because the nature of the residual waste product can vary greatly from facility to facility, which will likely affect PAH emissions. The type of auxiliary fuel used can also have a significant effect on PAH emissions from these facilities.

#### Source Location

Approximately 2.8 to 6.4 million 55-gallon drums are incinerated annually in the U.S. (U.S. EPA, 1994). This estimate is based on the assumptions that there are 23 to 26 incinerators currently in operation, each incinerator handles 500 to 1,000 drums per day, and each incinerator operates 5 days a week with 14 days down time for maintenance.

#### SECTION 4.3.6 REFERENCES

Galson Corporation. Source Emission Test Results for Drum Furnace/Afterburner. Galson Technical Services, Berkeley, California. Galson Project #SE-280. 1992.

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#### 4.3.7 Scrap Tire Incineration

Most facilities that burn tires use the tires to supplement a primary fuel, such as wood. This section, however, addresses those facilities that burn scrap tires as the only fuel. The primary purpose of these facilities is to recover energy from the combustion of scrap tires.

##### Process Description

The following process description is based on the operations at the Modesto Energy Facility in Westley, California, which is a dedicated tire-to-energy facility. This process should be applicable to most of these types of facilities because the technology is licensed to one company in the United States.

The Modesto facility consists of two whole-tire boilers that generate steam from the combustion of the scrap tires. Tires from a nearby supply pile are fed into a hopper located adjacent to the pile. Tires are then fed into the boilers at a rate of 350 to 400 tires per hour for each boiler. The boilers can accommodate tires as large as 4 feet in diameter made of rubber, fiberglass, polyester, and nylon.

The tires are burned on large reciprocating stoker grates in the combustion chamber at the bottom of the boilers. The grate configuration allows air flow above and below the tires, which aids in complete combustion. The boilers are operated above 2,000°F (1,093°C) to ensure complete combustion of organic compounds emitted by the burning tires. The heat generated by the burning of the tires causes the water contained in the pipes of the refractory brickwork that lines the boiler to turn into steam. The high-pressure steam is then forced through a turbine for the generation of power.

Three air pollution control techniques are used at the Modesto facility to control NO<sub>x</sub>, PM, and SO<sub>x</sub>. The PM control device, a fabric filter, likely has the most significant impact on particulate POM emissions. After exiting the boiler chamber and the NO<sub>x</sub> control system, exhaust gases pass through the large fabric filter.



## Emission Factors

PAHs have been measured in the post-control exhaust gas at the Modesto facility. Emission factors developed from these data are provided in Table 4.3.7-1. These factors were generated assuming a heating value of 300,000 Btu per tire. Emission data from other tire-to-energy facilities were not available; however, facilities that use similar technology would be expected to have PAH emissions in the same of order of magnitude as the Modesto facility.

## Source Location

The EPA's Office of Solid Waste has estimated that approximately 25.9 million scrap tires were incinerated in the United States in 1990 (U.S. EPA, 1992). This equates to approximately 10.7 percent of the 242 million scrap tires that were generated in 1990. The use of scrap tires as fuel increased significantly during the late 1980s, and is expected to continue to increase (U.S. EPA, 1992).

In December 1991, there were two operational, dedicated tire-to-energy facilities in the United States: the Modesto Energy Project in Westley, California, and the Exter Energy Company in Sterling, Connecticut. The Erie Energy Project, which was still in the planning stages when this document was written, was to be located at Lackawanna, New York. The total capacity for all three plants combined could approach almost 25 million tires per year (4.5 million at the Modesto plant, and 10 million each at the Exter and Erie plants) (U.S. EPA, 1991).

TABLE 4.3.7-1. PAH EMISSION FACTORS FOR SCRAP TIRE BURNING

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/million tires (g/million tires) <sup>a</sup>	Emission Factor Rating
5-03-001-02	Scrap Tire Incinerator	Fabric Filter	Benzo(b)fluoranthene	1.68E-03 (0.76)	E
			Acenaphthene	1.68E-03 (0.76)	E
			Anthracene	3.00E-03 (1.36)	E
			Fluoranthene	5.10E-03 (2.31)	E
			Fluorene	5.10E-03 (2.31)	E
			Naphthalene	3.60E-01 (163.30)	E
			Phenanthrene	1.68E-02 (7.62)	E
			Pyrene	6.60E-03 (2.99)	E

<sup>a</sup>Emission factors are expressed in lb (g) of pollutant emitted per million scrap tires incinerated.

Source: U.S. EPA, 1991.

#### SECTION 4.3.7 REFERENCES

U.S. Environmental Protection Agency. Summary of Markets for Scrap Tires. Office of Solid Waste, Washington, DC. EPA/530-SW-90-074B. 1992.

U.S. Environmental Protection Agency. Burning Tires for Fuel and Tire Pyrolysis: Air Implications. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/3-91-024. pp. 3-1 to 3-21. 1991.

#### 4.3.8 Landfill Waste Gas Flares

##### Process Description

A municipal solid waste (MSW) landfill unit is a discrete area of land or an excavation that receives household waste. An MSW landfill unit may also receive other types of wastes, such as commercial solid waste, nonhazardous sludge, and industrial solid waste (U.S. EPA, 1995). POM emissions from MSW landfills are expected to originate from the flaring of waste gas that evolves from the landfill. Waste gas evolves from the biodegradation process, vaporization, and chemical reactions at the landfill, and at some sites it is collected through a piping network and then burned at the top of vent pipes.

Landfill gas collection systems are either active or passive systems. Active collection systems provide a pressure gradient in order to extract landfill gas by use of mechanical blowers or compressors. Passive systems allow the natural pressure gradient created by the increase in landfill pressure from landfill gas generation to mobilize the gas for collection.

Landfill gas control and treatment options include (1) combustion of the landfill gas, and (2) purification of the landfill gas. Combustion practices producing POM emissions include techniques that do not recover energy (e.g., flares and thermal incinerators) and techniques that do recover energy and generate electricity from the combustion of the landfill gas (e.g., gas turbines and internal combustion engines). Boilers can also be employed to recover energy from landfill gas in the form of steam (U.S. EPA, 1995). The formation of POM from boilers, internal combustion engines and turbines are discussed in Sections 4.1.2, 4.2.1, and 4.2.2, respectively, of this report.

Flares involve an open combustion process that requires oxygen for combustion; the flares themselves can be open or enclosed. Thermal incinerators heat an organic chemical to a high enough temperature in the presence of sufficient oxygen to oxidize the chemical to CO<sub>2</sub> and water. Purification techniques can also be used to process raw landfill gas to pipeline quality natural gas by using adsorption, absorption, and membranes (U.S. EPA, 1994).

## Emission Factors

PAH emission factors for a landfill flare are presented in Table 4.3.8-1. The factors are based on a test conducted for a burner rated at 31 MMBtu/hr (Gj/hr). Combustion air is drawn into the base of the flare through dampered openings. Landfill gas is fed to the burner just above the dampered openings and combustion takes place inside the refractory lined flare. Test samples were taken from the flare exhaust. Emission factors were derived from the test samples based on the heat input of the waste gas (U.S. EPA, 1994).

Naphthalene, acenaphthene, fluorene, pyrene, chrysene, benzo(b)fluoranthene, benzo(e)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene were all found in the test sample, but not in significant quantities when compared to the blank. Measurable quantities of phenanthrene and fluoranthene were present above the blank values. Acenaphthalene, anthracene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene, perylene, and dibenz(a,h)anthracene were found in the test sample at the detection limit.

## Source Location

MSW management in the United States is dominated by disposal in landfills. Approximately 67 percent of solid waste is landfilled, 16 percent is incinerated, and 17 percent is recycled or composted. There were an estimated 5,345 active MSW landfills in the United States in 1992. In 1990, active landfills were receiving an estimated 130 million tons (118 million Mg) of waste annually, with 55 to 60 percent reported as household waste and 35 to 45 percent reported as commercial waste (U.S. EPA, 1995).

TABLE 4.3.8-1. PAH EMISSION FACTORS FOR LANDFILL FLARES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor (lb/MMBtu) <sup>a</sup>	Average Emission Factor (g/kj) <sup>a</sup>	Emission Factor Rating
5-02-006-01	Solid Waste Landfill (Waste Gas Flares)	Afterburner	Benz(a)anthracene	6.26E-11	2.69E-14	C
			Benzo(a)pyrene	1.14E-10	4.89E-14	C
			Benzo(k)fluoranthene	6.49E-11	2.78E-14	C
			Chrysene	2.97E-08	1.27E-11	C
			Dibenz(a,h)anthracene	2.77E-10	1.19E-13	C
			Indeno(1,2,3-cd)pyrene	5.83E-10	2.50E-13	C
			Acenaphthene	1.05E-07	4.50E-11	C
			Acenaphthylene	4.27E-08	1.83E-11	C
			Benzo(ghi)perylene	9.53E-10	4.09E-13	C
			Anthracene	2.32E-10	9.95E-14	C
			Fluoranthene	7.26E-07	3.11E-10	C
			Fluorene	1.50E-07	6.44E-11	C
			Naphthalene	1.00E-05	4.29E-09	C
			Phenanthrene	1.88E-06	8.07E-10	C
Pyrene	1.56E-08	6.69E-12	C			

<sup>a</sup>Emission factors are expressed in lb (g) of pollutant emitted per MMBtu (kj) of heat input into the burner.

Source: U.S. EPA, 1994.

#### SECTION 4.3.8 REFERENCES

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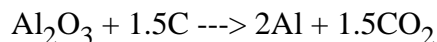
## 4.4 METAL INDUSTRY

### 4.4.1 Primary Aluminum Production

#### Process Description

All primary aluminum in the United States is produced by the Hall-Heroult process of electrolytic reduction of alumina. The general procedures for primary aluminum reduction are illustrated in Figure 4.4.1-1 (U.S. EPA, 1979). Aluminum reduction is carried out in shallow rectangular cells (pots) made of carbon-lined steel, with carbon blocks suspended above and extending down into the pot. The pots and carbon blocks serve as cathodes and anodes, respectively, for the electrolytical process (U.S. EPA, 1979; Siebert et al., 1978; Wallingford and Hee, 1985).

Cryolite ( $\text{Na}_3\text{AlF}_6$ ), a double fluoride salt of sodium and aluminum, serves as an electrolyte and a solvent for alumina. Alumina is added to and dissolves in the molten cryolite bath. The cells are heated and operated between 1,742 to 1,832°F (950 to 1,000°C) with heat that results from resistance between the electrodes. During the reduction process, the aluminum is deposited at the cathode where, because of its heavier weight ( $2.3 \text{ g/cm}^3$  versus  $2.1 \text{ g/cm}^3$  for cryolite), it remains as a molten metal layer underneath the cryolite. The cryolite bath thus also protects the aluminum from the atmosphere. The byproduct oxygen migrates to and combines with the consumable carbon anode to form  $\text{CO}_2$  and  $\text{CO}$ , which continually evolve from the cell. The basic reaction of the reduction process is (U.S. EPA, 1979):



Alumina and cryolite are periodically added to the bath to replenish material that is removed or consumed in normal operation. The weight ratio of sodium fluoride ( $\text{NaF}$ ) to aluminum fluoride ( $\text{AlF}_3$ ) in cryolite is 1.5. Fluorspar (calcium fluoride) may also be added to lower the bath's melting point. Periodically, the molten aluminum is siphoned or tapped from beneath the cryolite bath, moved in the molten state to holding furnaces in the casting area, and



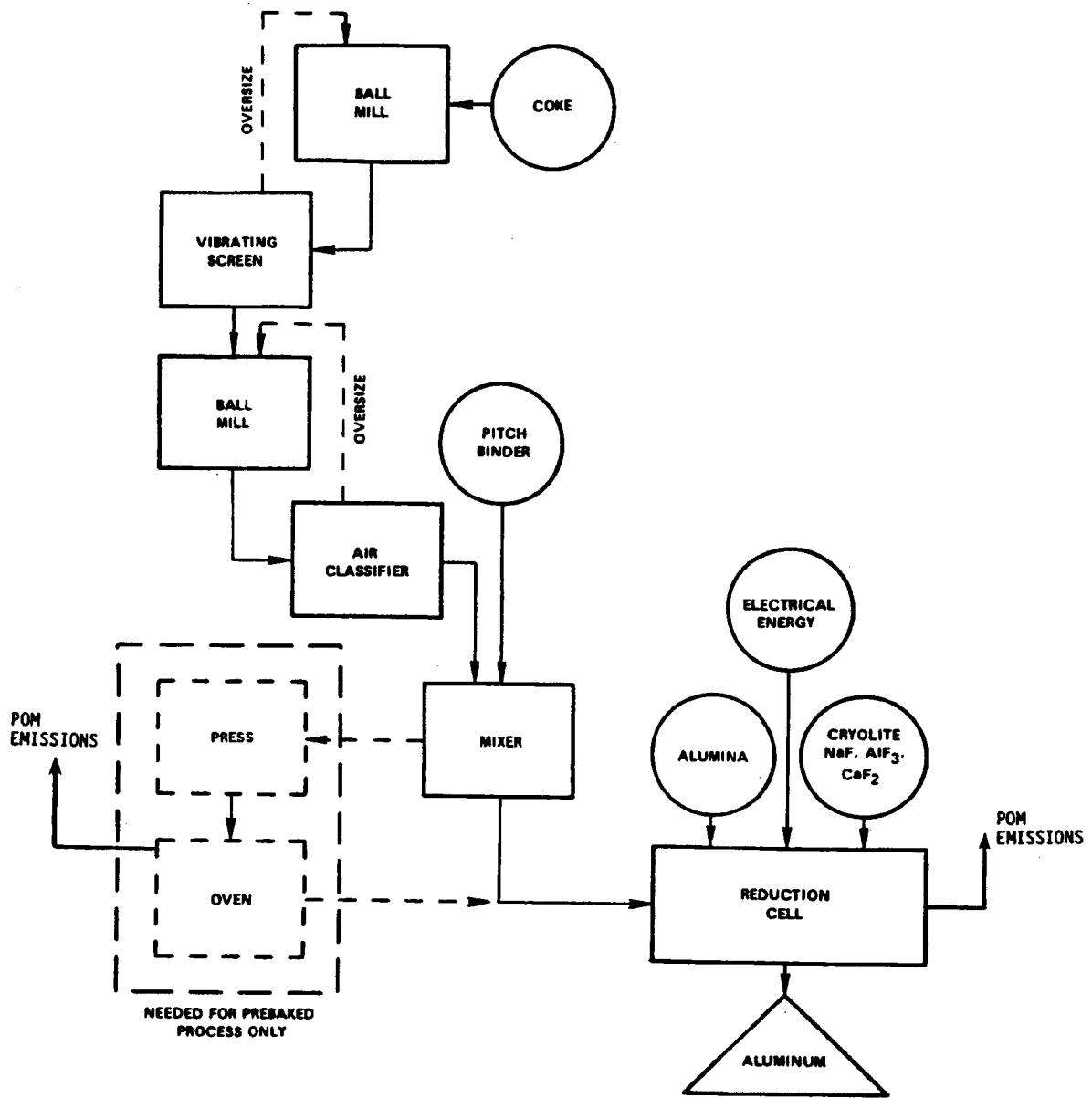


Figure 4.4.1-1. General Flow Diagram for Primary Aluminum Reduction

Source: U.S. EPA, 1979.

fluxed to remove trace impurities. The product aluminum is later tapped from the holding furnaces and cast into ingots or billets to await further processing or it is shipped as molten in insulated ladles (U.S. EPA, 1979).

The process of primary aluminum reduction is essentially one of materials handling. The true difference in the various process modifications used by the industry lies in the type of reduction cell used. Three types of reduction cells or pots are used in the United States: prebake, horizontal stud Soderberg, and vertical stud Soderberg (Figure 4.4.1-2). Prebake cells constitute the bulk of aluminum production (66 percent), followed by horizontal Soderbergs (21 percent), and vertical Soderbergs (13 percent) (U.S. EPA, 1979). Both Soderberg cells employ continuously formed consumable carbon anodes, where the anode paste is baked by the energy of the reduction cell itself. The prebake cell, as indicated by its name, employs a replaceable, consumable carbon anode, formed by baking in a separate facility called an anode bake plant, prior to its use in the cell.

The preparation and operation of the aluminum reduction cells is the primary source of potential POM emissions from primary aluminum production. The magnitude of POM emissions from a typical reduction plant is a function of the type of reduction cell used (Siebert et al., 1978). Prebaked cell anodes are made by curing the carbon contained in pitch and coke at relatively high temperatures ( $\sim 2,000^{\circ}\text{F}$  [ $\sim 1,100^{\circ}\text{C}$ ]). A flow diagram depicting the production of prebaked cells is shown in Figure 4.4.1-3. The high-temperature curing process can generate POM emissions. Potentially, POM compounds can be emitted from the prebake cell during the reduction process when the anodes are lowered into the reduction pot. However, POM emissions from reduction are expected to be much less than those from Soderberg cells because essentially all of the POM emissions have already been released during the preparation and baking of anodes (U.S. EPA, 1979; Wallingford and Hee, 1985; Strieter, 1996).

Soderberg cell anodes are continuously lowered and baked by conductive heat from the molten alumina bath rather than being premolded and baked. A coke and coal tar pitch paste is packed into a metal shell over the bath. As the baked anode at the bottom of the shell is consumed, more paste is added at the top of the shell. As the paste is consumed, potential POM

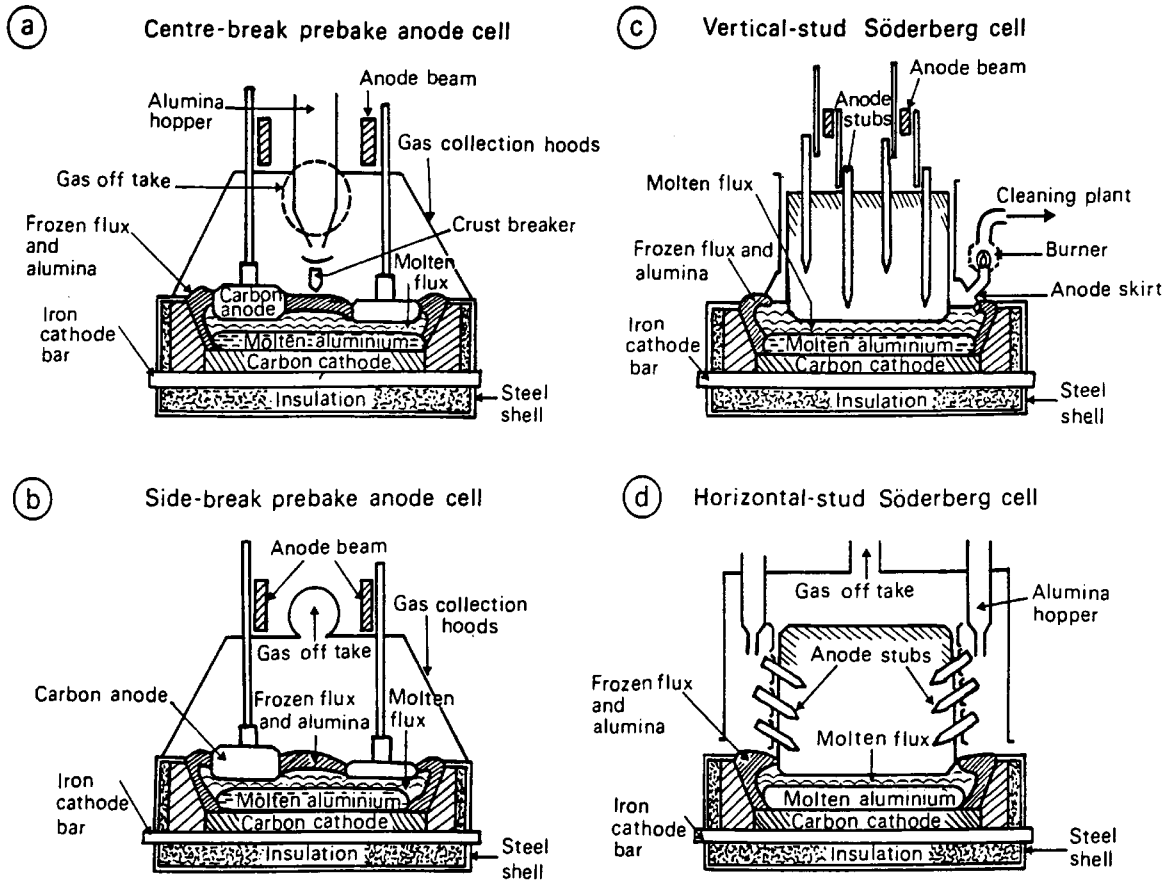
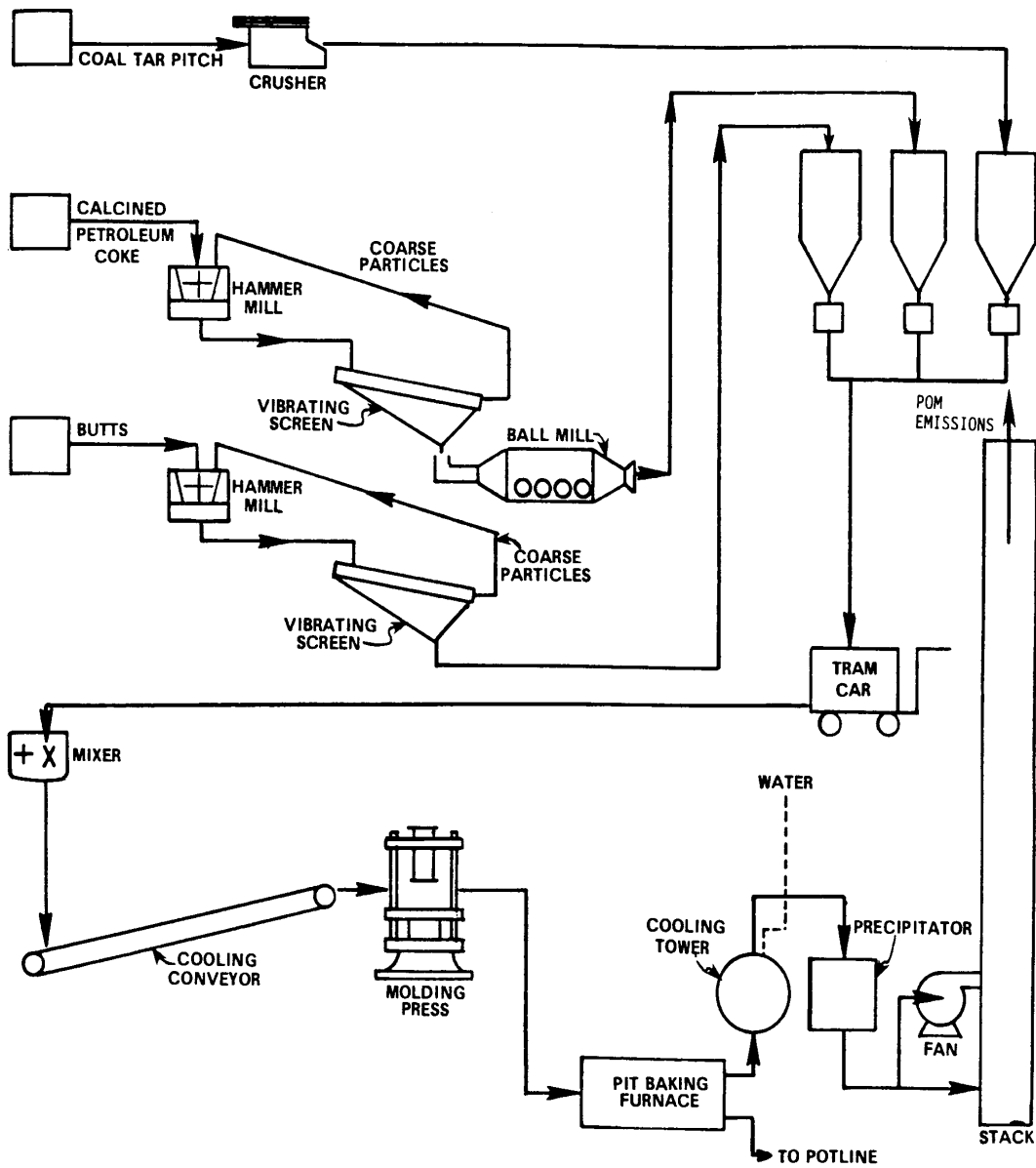


Figure 4.4.1-2. Types of Electrolytic Cells Used in Alumina Reduction

Source: IARC, 1984.



ERG\_POM\_4413.pre

Figure 4.4.1-3. Flow Diagram Depicting the Production of Prebaked Cells

Source: U.S. EPA, 1979.

emissions are released. Because the carbon paste is not baked prior to being placed in the pot, POM emissions from a Soderberg cell (horizontal or vertical stud) reduction operation have the potential to be much greater than those from a prebaked cell reduction operation.

An additional source of potential POM emissions associated with primary aluminum production is aluminum casthouse operations, or the pouring, cooling, and shakeout of aluminum castings (Gressel et al., 1988). Most commonly, aluminum foundries produce castings using green sand molds. The evaporative casting (EPC) process may be used to produce complex-shaped castings. In the EPC process, a low-density polystyrene foam facsimile of the part to be cast is formed, coated with refractory wash, and packed in a flask with dry unbonded sand. Introduction of molten metal causes the polystyrene to evaporate. Use of the EPC process in the foundry industry has the potential for expansion because of its low cost and versatility (Gressel et al., 1988).

Emissions control at primary aluminum reduction facilities (cell rooms or pot rooms) is intended primarily for fluoride removal and involves efficient emissions capture and removal. Emissions capture is generally accomplished by using precisely designed hooding and ducting systems on reduction cells. The term hooding includes the use of classical draft hoods and the use of movable doors, enclosures, and skirts. Primary emissions removal is achieved through the use of dry scrubbing systems or wet scrubber/ESP systems. Two types of dry scrubbing systems, fluidized-bed and injected alumina, are found in the industry, and both contain baghouse equipment to collect PM from the chemical absorption scrubbing process. These baghouses would be effective in removing particulate POM in the emission stream.

Standard design spray tower wet scrubbers and wet ESPs used in the series are also effective primary control systems at aluminum reduction facilities. The ability of the combination wet scrubbing/precipitation system to remove particulate POM should be equal to that of the dry scrubbing/baghouses. In addition to being a primary control system for cell room emissions, wet scrubbers are also used in some facilities as the primary control system for producing prebake anodes (U.S. EPA, 1979; Strieter, 1996).

In some primary aluminum installations, secondary control systems are used. The predominant secondary system is a spray screen scrubber followed by a mist eliminator. The term spray screen scrubber is applied to wet scrubbers in which the scrubbing liquor is sprayed into a gas stream and onto screens or open-mesh filters enclosed in a plenum chamber (U.S. EPA, 1979). The use of spray screen wet scrubbers for secondary emission control only occurs at a few facilities. Rather, the predominant emission control technology currently in use is to provide better capture of emissions at the reduction cells through hooding and shielding improvements for the primary control system (Strieter, 1996).

### Emission Factors

Emission factors were developed for five primary aluminum production processes. Clement International Corporation presented PAH emissions data for a primary aluminum smelter in the United States, which was based on the average of five testing programs conducted from 1985 to 1991 (Clement International Corporation, 1992; State of Washington DOE, 1985). Sampling and analytical methods were used to quantify both particulate and vaporous PAHs. The facility operated three potlines containing 280 pots with a production capacity of approximately 200 tons per day. A separate manufacturing building was used to mix coke and coal tar pitch into a dense paste to replenish the consumable carbon anode used in the reduction process. The report indicates that there were no significant process changes during the test data averaging period. PAH emissions were quantified for the paste preparation plant, the horizontal stud Soderberg cells following a dry scrubber, and from the potroom roof vents.

Emissions data were also obtained from source testing performed for the development of the Primary Aluminum Production MACT. The final MACT rule was published on September 19, 1997. The emission factors are based on testing at four aluminum facilities in 1994 (AmTest Air Quality, Inc., 1994a; 1994b; 1994c; 1994d). The testing for POM included the use of a surrogate measure based on extracting the front and back half catches of a modified Method 5 sampling train with methylene chloride. The compounds extracted by the methylene chloride include the POM species of interest as well as some other compounds. In addition, the individual POM species typically found in the pitch were quantified.

PAH emissions were quantified for a paste preparation plant (with scrubbers and baghouse), vertical stud Soderberg cells (followed by wet and dry scrubbers), horizontal stud Soderberg cells (followed by dry scrubbers), secondary roof emissions (wet and dry scrubbers), and an anode bake furnace with dry scrubber.

Tables 4.4.1-1 to 4.4.1-9 present the emission factors developed from the Clement and MACT tests. Emission factors from the two data sets were averaged where overlap between data points existed.

Pot gas emissions are controlled with a dry scrubber system, forcing the gases and dusts through a bed of finely powdered alumina. Organics are adsorbed onto the alumina particles in the dry scrubber, and alumina and other dust particles are captured by impaction. PM escaping the scrubber is entrained by a baghouse in series. The alumina scrubbing medium and dust collected in the baghouse are periodically recycled to the production process.

A toxic air emissions inventory conducted in Canada and the United States reported PAH emission factors for primary aluminum reduction using prebake cells

TABLE 4.4.1-1. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION:  
PASTE PREPARATION, UNCONTROLLED

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-99	Paste Preparation Plant	None	Benz(a)anthracene	2.57E-04 (1.28E-04)	D
			Benzo(a)pyrene	9.53E-06 (4.74E-06)	D
			Benzo(b)fluoranthene	9.53E-06 (4.74E-06)	D
			Benzo(k)fluoranthene	9.53E-06 (4.74E-06)	D
			Chrysene	1.24E-04 (6.16E-05)	D
			Dibenz(a,h)anthracene	9.53E-06 (4.74E-06)	D
			Indeno(1,2,3-cd)pyrene	9.53E-06 (4.74E-06)	D
			Acenaphthene	6.04E-02 (3.00E-02)	D
			Acenaphthylene	2.86E-05 (1.42E-05)	D
			Anthracene	7.15E-03 (3.55E-03)	D
			Benzo(ghi)perylene	9.53E-06 (4.74E-06)	D
			Fluoranthene	2.36E-02 1.18E-02	D



TABLE 4.4.1-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-99 (continued)	Paste Preparation Plant (continued)	None	Fluorene	1.76E-02 (8.73E-03)	D
			Naphthalene	1.64E-02 (8.18E-03)	D
			Phenanthrene	4.85E-02 (2.41E-02)	D
			Pyrene	4.48E-04 (2.23E-04)	D
			Benzo(e)pyrene	9.53E-06 (4.74E-06)	D
			Dibenz(a,e)pyrene	9.53E-06 (4.74E-06)	D
			Dibenz(a,i)pyrene	9.53E-06 (4.74E-06)	D
			Dibenz(a,h)pyrene	9.53E-06 (4.74E-06)	D

<sup>a</sup>Emission factors are in lb/(kg) of pollutant emitted per ton (Mg) of aluminum produced.

Source: Clement International Corporation, 1992.

TABLE 4.4.1-2. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION:  
PASTE PREPARATION, BAGHOUSE CONTROLLED

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-99	Paste Preparation Plant	Baghouse	Benz(a)anthracene	1.2E-06 (6.00E-07)	U <sup>b</sup>
			Benzo(a)pyrene	1.1E-06 (5.50E-07)	U <sup>b</sup>
			Benzo(b)fluoranthene	2.2E-06 (1.1E-06)	U <sup>b</sup>
			Benzo(k)fluoranthene	7.5E-07 (3.75E-07)	U <sup>b</sup>
			Chrysene	1.8E-06 (9.0E-07)	U <sup>b</sup>
			Dibenz(a,h)anthracene	4.1E-07 (2.05E-07)	U <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	9.4E-07 (4.7E-07)	U <sup>b</sup>
			Acenaphthene	4.1E-07 (2.05E-07)	U <sup>b</sup>
			Acenaphthylene	2.2E-07 (1.1E-06)	U <sup>b</sup>
			Anthracene	2.8E-07 (1.40E-07)	U <sup>b</sup>
			Benzo(ghi)perylene	8.7E-07 (4.35E-07)	U <sup>b</sup>
			Fluoranthene	2.3E-06 1.15E-06	U <sup>b</sup>

4-200

(continued)

TABLE 4.4.1-2. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-99 (continued)	Paste Preparation Plant (continued)	Baghouse (continued)	Fluorene	3.5E-07 (1.75E-07)	U <sup>b</sup>
			Naphthalene	5.7E-07 (2.85E-07)	U <sup>b</sup>
			Phenanthrene	1.2E-06 (6.00E-07)	U <sup>b</sup>
			Pyrene	2.1E-06 (1.05E-06)	U <sup>b</sup>
			Benzo(e)pyrene	1.0E-06 (5.00E-07)	U <sup>b</sup>
			2-Chloronaphthalene	3.7E-07 (1.85E-07)	U <sup>b</sup>
			2-Methylnaphthalene	4.5E-07 (2.25E-07)	U <sup>b</sup>
			Perylene	4.7E-07 (2.35E-07)	U <sup>b</sup>

<sup>a</sup>Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of paste produced.

<sup>b</sup>Factor rating of “U” is not indicative of poor data, but reflects the fact that source test reports were not available for extensive review prior to L&E publication.

Source: AmTest Air Quality, Inc., 1994b; Entropy, Inc., 1994.

TABLE 4.4.1-3. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION:  
PASTE PREPARATION, DRY SCRUBBER CONTROLLED

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-99	Paste Preparation Plant	Dry Scrubber	Benz(a)anthracene	1.55E-05 (7.75E-06)	U <sup>b</sup>
			Benzo(a)pyrene	8.10E-07 (4.05E-07)	U <sup>b</sup>
			Benzo(b)fluoranthene	1.47E-06 (7.35E-07)	U <sup>b</sup>
			Benzo(k)fluoranthene	7.95E-07 (3.98E-07)	U <sup>b</sup>
			Chrysene	1.08E-05 (5.40E-06)	U <sup>b</sup>
			Dibenz(a,h)anthracene	3.53E-07 (1.76E-07)	U <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	2.78E-07 (1.39E-07)	U <sup>b</sup>
			Acenaphthene	1.02E-03 (5.08E-04)	U <sup>b</sup>
			Acenaphthylene	1.02E-05 (5.09E-06)	U <sup>b</sup>
			Anthracene	2.55E-04 (1.27E-04)	U <sup>b</sup>
			Benzo(ghi)perylene	2.48E-07 (1.24E-07)	U <sup>b</sup>
			Fluoranthene	5.26E-04 (2.63E-04)	U <sup>b</sup>

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(continued)

TABLE 4.4.1-3. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-99 (continued)	Paste Preparation Plant (continued)	Dry Scrubber (continued)	Fluorene	1.01E-03 (5.03E-04)	U <sup>b</sup>
			Naphthalene	4.45E-06 (2.23E-06)	U <sup>b</sup>
			Phenanthrene	1.56E-03 (7.78E-04)	U <sup>b</sup>
			Pyrene	2.16E-04 (1.08E-04)	U <sup>b</sup>
			Carbazole	1.00E-04 (5.00E-05)	U <sup>b</sup>
			2-Methylnaphthalene	5.95E-06 (2.98E-06)	U <sup>b</sup>
			Benzo(e)pyrene	5.10E-07 (2.55E-07)	U <sup>b</sup>

<sup>a</sup>Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of paste produced.

<sup>b</sup>Factor rating of "U" is not indicative of poor data, but reflects the fact that source test reports were not available for extensive review prior to L&E publication.

Source: AmTest Air Quality, Inc., 1994b; Entropy, Inc., 1994.

TABLE 4.4.1-4. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION:  
HORIZONTAL-STUD SODERBERG CELLS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg)	Emission Factor Rating
3-03-001-02	Horizontal Soderberg Cell	Dry Scrubber	Benz(a)anthracene	2.05E-03 (1.02E-03)	4.00E-04 - 3.69E-03 (2.00E-04 - 1.85E-03)	U <sup>b</sup>
			Benzo(a)pyrene	1.24E-03 (6.20E-04)	1.00E-04 - 2.38E-03 (5.00E-05 - 1.19E-03)	U <sup>b</sup>
			Benzo(b)fluoranthene	1.34E-03 (6.70E-04)	3.00E-04 - 2.38E-03 (1.50E-04 - 1.19E-03)	U <sup>b</sup>
			Benzo(k)fluoranthene	1.20E-03 (6.00E-04)	1.00E-04 - 2.30E-03 (5.00E-05 - 1.15E-03)	U <sup>b</sup>
			Chrysene	3.20E-03 (1.60E-03)	1.00E-03 - 5.40E-03 (5.00E-04 - 2.70E-03)	U <sup>b</sup>
			Dibenz(a,h)anthracene	2.10E-03 (1.05E-03)	2.00E-05 - 4.18E-03 (1.00E-05 - 2.09E-03)	U <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	2.14E-03 (1.07E-03)	1.00E-04 - 4.18E-03 (5.00E-05 - 2.09E-03)	U <sup>b</sup>
			Acenaphthene	2.15E-01 (1.08E-01)	1.00E-03 - 4.29E-01 (5.00E-04 - 2.15E-01)	U <sup>b</sup>
			Acenaphthylene	1.27E-02 (6.35E-03)	1.00E-04 - 2.53E-02 (5.00E-05 - 1.27E-02)	U <sup>b</sup>
			Anthracene	1.96E-01 (9.78E-02)	4.00E-03 - 3.87E-01 (2.00E-03 - 1.94E-01)	U <sup>b</sup>
			Benzo(ghi)perylene	2.14E-03 (1.07E-03)	1.00E-04 - 4.18E-03 (5.00E-05 - 2.09E-03)	U <sup>b</sup>
			Fluoranthene	1.08E-01 (5.38E-02)	3.50E-02 - 1.80E-01 (1.75E-02 - 9.00E-02)	U <sup>b</sup>

4-204

(continued)

TABLE 4.4.1-4. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg)	Emission Factor Rating
3-03-001-02 (continued)	Horizontal Soderberg Cell (continued)	Dry Scrubber (continued)	Fluorene	1.43E-01 (7.15E-02)	2.90E-02 - 2.57E-01 (1.45E-02 - 1.29E-01)	U <sup>b</sup>
			Naphthalene	2.07E-01 (1.04E-01)	2.00E-04 - 4.14E-01 (1.00E-04 - 2.07E-01)	U <sup>b</sup>
			Phenanthrene	6.06E-01 (3.03E-01)	3.20E-01 - 8.91E-01 (1.60E-01 - 4.46E-01)	U <sup>b</sup>
			Pyrene	8.40E-02 (4.20E-02)	2.80E-02 - 1.40E-01 (1.40E-02 - 7.00E-02)	U <sup>b</sup>
			Benzo(e)pyrene	4.18E-03 (2.09E-03)	1.00E-04 - 4.18E-03 (5.00E-05 - 2.09E-03)	U <sup>b</sup>
			Dibenz(a,e)pyrene	4.60E-03 (2.29E-03)	---	U <sup>b</sup>
			Dibenz(a,i)pyrene	4.60E-03 (2.29E-03)	---	U <sup>b</sup>
			Dibenz(a,h)pyrene	4.60E-03 (2.29E-03)	---	U <sup>b</sup>
			Carbazole	1.00E-03 (5.00E-04)	---	U <sup>b</sup>
			2-Methylnaphthalene	1.00E-03 (5.00E-04)	---	U <sup>b</sup>

<sup>a</sup>Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of aluminum produced.

<sup>b</sup>Factor rating of "U" is not indicative of poor data, but reflects the fact that source test reports were not available for extensive review prior to L&E publication.

Source: Clement International Corporation, 1992; AmTest Air Quality, Inc., 1994a.

"---" means no data available.

TABLE 4.4.1-5. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION:  
VERTICAL-STUD SODERBERG CELLS, DRY SCRUBBER CONTROLLED

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-02	Vertical Soderberg Cell	Dry Scrubber	Benz(a)anthracene	9.4E-06 (4.70E-06)	U <sup>b</sup>
			Benzo(a)pyrene	4.2E-06 (2.10E-06)	U <sup>b</sup>
			Benzo(b)fluoranthene	1.2E-05 (6.00E-06)	U <sup>b</sup>
			Benzo(k)fluoranthene	4.4E-06 (2.20E-06)	U <sup>b</sup>
			Chrysene	2.0E-05 (1.00E-05)	U <sup>b</sup>
			Dibenz(a,h)anthracene	4.5E-06 (2.25E-06)	U <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	4.4E-06 (2.2E-06)	U <sup>b</sup>
			Acenaphthene	5.7E-06 (2.85E-06)	U <sup>b</sup>
			Acenaphthylene	3.4E-06 (1.70E-06)	U <sup>b</sup>
			Anthracene	3.0E-06 (1.50E-06)	U <sup>b</sup>
			Benzo(ghi)perylene	4.7E-06 (2.35E-06)	U <sup>b</sup>
			Fluoranthene	2.8E-04 (1.4E-04)	U <sup>b</sup>

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(continued)



TABLE 4.4.1-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-02 (continued)	Vertical Soderberg Cell (continued)	Dry Scrubber (continued)	Fluorene	1.1E-05 (5.50E-06)	U <sup>b</sup>
			Naphthalene	2.7E-05 (1.35E-05)	U <sup>b</sup>
			Phenanthrene	3.0E-04 (1.50E-04)	U <sup>b</sup>
			Pyrene	1.4E-04 (7.00E-05)	U <sup>b</sup>
			Benzo(e)pyrene	4.6E-06 (2.3E-06)	U <sup>b</sup>
			2-Chloronaphthalene	5.5E-06 (2.75E-06)	U <sup>b</sup>
			2-Methylnaphthalene	4.5E-06 (2.25E-06)	U <sup>b</sup>
			Perylene	4.2E-06 (2.1E-06)	U <sup>b</sup>

<sup>a</sup>Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of aluminum produced.

<sup>b</sup>Factor rating of "U" is not indicative of poor data, but reflects the fact that source test reports were not available for extensive review prior to L&E publication.

Source: Entropy, Inc., 1994.

TABLE 4.4.1-6. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION:  
VERTICAL-STUD SODERBERG CELLS, WET SCRUBBER WITH DRY SCRUBBER CONTROLLED

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-02	Vertical Soderberg Cell	Wet Scrubber following Dry Scrubber	Benz(a)anthracene	6.6E-06 (3.3E-06)	U <sup>b</sup>
			Benzo(a)pyrene	4.8E-06 (2.40E-06)	U <sup>b</sup>
			Benzo(b)fluoranthene	1.0E-05 (5.00E-06)	U <sup>b</sup>
			Benzo(k)fluoranthene	4.9E-06 (2.45E-06)	U <sup>b</sup>
			Chrysene	2.7E-05 (1.35E-05)	U <sup>b</sup>
			Dibenz(a,h)anthracene	5.0E-06 (2.50E-06)	U <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	4.7E-06 (2.35E-06)	U <sup>b</sup>
			Acenaphthene	6.5E-06 (3.25E-06)	U <sup>b</sup>
			Acenaphthylene	3.7E-06 (1.85E-06)	U <sup>b</sup>
			Anthracene	3.6E-06 (1.80E-06)	U <sup>b</sup>
			Benzo(ghi)perylene	5.3E-06 (2.65E-06)	U <sup>b</sup>
Fluoranthene	1.1E-04 (5.50E-05)	U <sup>b</sup>			

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(continued)

TABLE 4.4.1-6. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-02 (continued)	Vertical Soderberg Cell (continued)	Wet Scrubber following Dry Scrubber (continued)	Fluorene	6.8E-06 (3.4E-06)	U <sup>b</sup>
			Naphthalene	4.6E-05 (2.30E-05)	U <sup>b</sup>
			Phenanthrene	1.2E-04 (6.00E-05)	U <sup>b</sup>
			Pyrene	1.8E-05 (9.00E-06)	U <sup>b</sup>
			Benzo(e)pyrene	4.8E-06 (2.4E-06)	U <sup>b</sup>
			2-Chloronaphthalene	9.2E-06 (4.60E-06)	U <sup>b</sup>
			2-Methylnaphthalene	5.7E-06 (2.85E-06)	U <sup>b</sup>
			Perylene	4.8E-06 (2.4E-06)	U <sup>b</sup>

<sup>a</sup>Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of aluminum produced.

<sup>b</sup>Factor rating of "U" is not indicative of poor data, but reflects the fact that source test reports were not available for extensive review prior to L&E publication.

Source: Entropy, Inc., 1994.

TABLE 4.4.1-7. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION: POTROOMS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-07	Potroom Roof Vents	None	Benz(a)anthracene	7.23E-02 (3.59E-02)	D
			Benzo(a)pyrene	3.63E-02 (1.80E-02)	D
			Benzo(b)fluoranthene	8.07E-02 (4.01E-02)	D
			Benzo(k)fluoranthene	3.79E-02 (1.88E-02)	D
			Chrysene	1.90E-01 (9.45E-02)	D
			Dibenz(a,h)anthracene	1.21E-02 (6.01E-03)	D
			Indeno(1,2,3-cd)pyrene	1.64E-02 (8.10E-03)	D
			Acenaphthene	1.53E-01 (7.60E-02)	D
			Acenaphthylene	3.70E-02 (1.84E-02)	D
			Anthracene	6.43E-002 (3.20E-02)	D
			Benzo(ghi)perylene	1.73E-02 (8.60E-03)	D
			Fluoranthene	5.50E-01 (2.73E-01)	D

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(continued)

TABLE 4.4.1-7. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-07 (continued)	Potroom Roof Vents (continued)	None	Fluorene	7.51E-02 (3.73E-02)	D
			Naphthalene	1.31E-01 (6.49E-02)	D
			Phenanthrene	9.40E-01 (4.68E-01)	D
			Pyrene	3.79E-01 (1.88E-01)	D
			Benzo(e)pyrene	4.58E-02 (2.28E-02)	D
			Dibenz(a,e)pyrene	1.05E-02 (5.22E-03)	D
			Dibenz(a,i)pyrene	1.05E-02 (5.22E-03)	D
			Dibenz(a,h)pyrene	1.05E-02 (5.22E-03)	D

<sup>a</sup>Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of aluminum produced.

Source: Clement International Corporation, 1992.

TABLE 4.4.1-8. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION:  
SECONDARY ROOF VENTS, DRY SCRUBBER CONTROLLED

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-07	Secondary Roof Vents	Dry Scrubber	Benz(a)anthracene	5.01E-03 (2.51E-03)	U <sup>b</sup>
			Benzo(a)pyrene	1.52E-03 (7.61E-04)	U <sup>b</sup>
			Benzo(b)fluoranthene	5.78E-03 (2.89E-03)	U <sup>b</sup>
			Benzo(k)fluoranthene	1.77E-03 (8.84E-04)	U <sup>b</sup>
			Chrysene	1.28E-02 (6.42E-03)	U <sup>b</sup>
			Dibenz(a,h)anthracene	5.22E-04 (2.61E-04)	U <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	1.26E-03 (6.32E-04)	U <sup>b</sup>
			Acenaphthene	7.21E-05 (3.61E-05)	U <sup>b</sup>
			Anthracene	1.02E-03 (5.11E-04)	U <sup>b</sup>
			Benzo(ghi)perylene	1.26E-03 (6.31E-04)	U <sup>b</sup>
			Fluoranthene	2.40E-02 (1.20E-02)	U <sup>b</sup>
Fluorene	1.20E-04 (5.98E-05)	U <sup>b</sup>			

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(continued)

TABLE 4.4.1-8. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-07 (continued)	Secondary Roof Vents (continued)	Dry Scrubber (continued)	Naphthalene	7.21E-05 (3.61E-05)	U <sup>b</sup>
			Phenanthrene	9.01E-03 (4.50E-03)	U <sup>b</sup>
			Pyrene	1.90E-02 (9.50E-03)	U <sup>b</sup>
			Carbazole	1.28E-03 (6.42E-04)	U <sup>b</sup>
			2-Methylnaphthalene	9.71E-05 (4.86E-05)	
			2-Chloronaphthalene	5.96E-05 (2.98E-05)	U <sup>b</sup>

<sup>a</sup>Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of aluminum produced.

<sup>b</sup>Factor rating of “U” is not indicative of poor data, but reflects the fact that source test reports were not available for extensive review prior to L&E publication.

Source: AmTest Air Quality, Inc., 1994a; 1994b; 1994c.

TABLE 4.4.1-9. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION:  
SECONDARY ROOF VENTS, WET SCRUBBER CONTROLLED

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-07	Secondary Roof Vents	Wet Scrubber	Benz(a)anthracene	2.30E-02 (1.15E-02)	U <sup>b</sup>
			Benzo(a)pyrene	1.20E-02 (6.00E-03)	U <sup>b</sup>
			Benzo(b)fluoranthene	3.00E-02 (1.50E-02)	U <sup>b</sup>
			Benzo(k)fluoranthene	8.40E-03 (4.20E-03)	U <sup>b</sup>
			Chrysene	4.00E-02 (2.00E-02)	U <sup>b</sup>
			Dibenz(a,h)anthracene	3.00E-03 (1.50E-03)	U <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	6.60E-03 (3.30E-03)	U <sup>b</sup>
			Acenaphthene	1.30E-03 (6.50E-04)	U <sup>b</sup>
			Anthracene	1.90E-02 (9.50E-03)	U <sup>b</sup>
			Benzo(ghi)perylene	8.50E-03 (4.25E-03)	U <sup>b</sup>
			Fluoranthene	1.20E-01 (6.00E-02)	U <sup>b</sup>
			Fluorene	4.70E-03 (2.35E-03)	U <sup>b</sup>

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(continued)



TABLE 4.4.1-9. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-07	Potroom Roof Vents	None	Phenanthrene	1.20E-01 (6.00E-02)	U <sup>b</sup>
			Pyrene	9.30E-02 (4.65E-02)	U <sup>b</sup>
			Benzo(e)pyrene	1.30E-02 (6.50E-03)	U <sup>b</sup>
			Perylene	3.10E-03 (1.55E-03)	U <sup>b</sup>

<sup>a</sup>Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of aluminum produced.

<sup>b</sup>Factor rating of “U” is not indicative of poor data, but reflects the fact that source test reports were not available for extensive review prior to L&E publication.

Source: Entropy, Inc., 1994.

(Johnson et al., 1990). The emission factor data came from a 1986 study of solid adsorber collection devices (Houle, 1986). The tested process was controlled with dry scrubbers. These data and those from the proposed MACT rule are presented in Table 4.4.1-10.

The MACT emission factors for two anode bake furnaces controlled by dry alumina scrubbers are presented in Table 4.4.1-11. Emissions from prebake cell preparation were not quantified.

Total PAH emission factors (the reference does not present individual PAH species or indicate exactly which PAH species are included in “total PAH”) from horizontal and vertical Soderberg reduction cells at a primary aluminum smelter were reported in a Swedish test report (Alfheim and Wikstrom, 1984). Total PAH emissions from the vertical Soderberg process (from pot gas dry scrubber and building ventilation) were 1.54 lb/ton (0.7 kg/ton), as opposed to 9.68 lb/ton (4.4 kg/ton) from the horizontal Soderberg process. The PAH emissions of the horizontal Soderberg process exhibited a higher fraction in the particulate phase than in the vapor phase. Conversely, PAH emissions from the vertical Soderberg process were predominantly in vapor form (Alfheim and Wikstrom, 1984).

Emission factors for the pouring, cooling, and shakeout of aluminum castings were reported (Gressel et al., 1988). A pilot test plant was engineered to quantify emissions of aerosol and gaseous PAHs from the green sand and evaporative casting (EPC) process. Emission factors for both processes are presented in Table 4.4.1-12.

#### Source Locations

As of December 1992, there were 23 primary aluminum reduction plants in the United States operated by 13 different companies. Washington State has seven plants, the most of any state in the country. A complete list of all 23 facilities is given in Table 4.4.1-13 (Plunkert and Sehnke, 1993).

TABLE 4.4.1-10. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION: PREBAKED CELL

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg)	Emission Factor Rating
3-03-001-01	Prebaked Anode Cell	Dry Scrubber	Benz(a)anthracene	1.26E-02 (6.29E-03)	3.80E-05 - 3.76E-02 (1.90E-05 - 1.88E-02)	U <sup>b</sup>
			Benzo(a)pyrene	5.74E-03 (2.87E-03)	1.00E-05 - 1.72E-02 (5.00E-06 - 8.60E-03)	U <sup>b</sup>
			Benzo(a)fluoranthene	1.94E-02 (9.70E-03)	1.00E-05 - 5.82E-02 (5.00E-06 - 2.91E-02)	U <sup>b</sup>
			Chrysene	1.79E-02 (8.93E-03)	8.20E-05 - 5.32E-02 (4.10E-05 - 2.66E-02)	U <sup>b</sup>
			Dibenz(a,h)anthracene	1.14E-03 (5.70E-04)	5.00E-06 - 3.40E-03 (2.50E-06 - 1.70E-03)	U <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	1.94E-03 (9.70E-04)	1.00E-05 - 8.80E-03 (5.00E-06 - 4.40E-03)	U <sup>b</sup>
			Acenaphthylene	5.41E-03 (2.71E-03)	1.00E-05 - 1.62E-02 (5.00E-06 - 8.10E-03)	U <sup>b</sup>
			Anthracene and Phenanthrene	5.18E-02 (2.59E-02)	1.00E-05 - 1.55E-01 (5.00E-06 - 7.75E-02)	U <sup>b</sup>
			Benzo(ghi)perylene	2.74E-03 (1.37E-03)	1.00E-05 - 8.20E-03 (5.00E-06 - 4.10E-03)	U <sup>b</sup>
			Fluoranthene	4.94E-02 (2.47E-02)	4.70E-05 - 1.48E-01 (2.35E-05 - 7.40E-02)	U <sup>b</sup>
			Fluorene	1.28E-03 (6.40E-04)	1.00E-05 - 3.80E-03 (5.00E-06 - 1.90E-03)	U <sup>b</sup>
			Naphthalene	2.00E-05 (1.00E-05)	1.00E-05 - 3.00E-05 (5.00E-06 - 1.50E-05)	U <sup>b</sup>

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(continued)

TABLE 4.4.1-10. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg)	Emission Factor Rating
3-03-001-01 (continued)	Prebaked Anode Cell (continued)	Dry Scrubber (continued)	Pyrene	4.14E-02 (2.07E-02)	4.10E-05 - 1.24E-01 (2.05E-05 - 6.20E-02)	U <sup>b</sup>
			Benzo(e)pyrene	2.68E-02 (1.34E-02)	---	U <sup>b</sup>
			2-Methylnaphthalene	3.00E-05 (1.50E-05)	1.00E-05 - 5.00E-05 (5.00E-06 - 2.50E-05)	U <sup>b</sup>
			Retene	1.50E-05 (7.50E-06)	1.00E-05 - 2.00E-05 (5.00E-06 - 1.00E-05)	U <sup>b</sup>

<sup>a</sup>Emission factors are in lb (kg) pollutant emitted per ton (Mg) of aluminum produced.

<sup>b</sup>Factor rating of “U” is not indicative of poor data, but reflects the fact that source test reports were not available for extensive review prior to L&E publication.

Source: Johnson et al., 1990; AmTest Air Quality, Inc., 1994c; AmTest Air Quality, Inc., 1994b.

“---” means data not available.

TABLE 4.4.1-11. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM PRODUCTION:  
ANODE BAKE FURNACE

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-05	Anode Bake Furnace	Dry Scrubber	Benz(a)anthracene	5.75E-05 (2.88E-05)	U <sup>b</sup>
			Benzo(a)pyrene	5.80E-05 (2.90E-05)	U <sup>b</sup>
			Benzo(b)fluoranthene	5.42E-04 (2.71E-04)	U <sup>b</sup>
			Benzo(k)fluoranthene	1.12E-04 (5.60E-05)	U <sup>b</sup>
			Chrysene	5.60E-04 (2.80E-04)	U <sup>b</sup>
			Dibenz(a,h)anthracene	5.36E-05 (2.68E-05)	U <sup>b</sup>
			Indeno(1,2,3-cd)pyrene	2.12E-04 (1.06E-04)	U <sup>b</sup>
			Acenaphthene	5.95E-06 (2.98E-06)	U <sup>b</sup>
			Acenaphthylene	1.10E-05 (5.48E-06)	U <sup>b</sup>
			Anthracene	2.98E-05 (1.49E-05)	U <sup>b</sup>
			Phenanthrene	1.49E-02 (7.45E-03)	U <sup>b</sup>
			Benzo(ghi)perylene	5.10E-04 (2.55E-04)	U <sup>b</sup>

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(continued)

TABLE 4.4.1-11. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-001-05 (continued)	Anode Baked Furnace (continued)	Dry Scrubber (continued)	Fluoranthene	3.75E-03 (1.88E-03)	U <sup>b</sup>
			Fluorene	5.44E-04 (2.72E-04)	U <sup>b</sup>
			Naphthalene	1.39E-05 (6.95E-06)	U <sup>b</sup>
			Pyrene	6.80E-04 (3.40E-04)	U <sup>b</sup>
			Carbazole	2.20E-05 (1.10E-05)	U <sup>b</sup>
			2-Methylnaphthalene	1.10E-05 (5.48E-06)	U <sup>b</sup>

<sup>a</sup>Emission factors are in lb (kg) pollutant emitted per ton (Mg) of anode produced.

<sup>b</sup>Factor rating of "U" is not indicative of poor data, but reflects the fact that source test reports were not available for extensive review prior to L&E publication.

Source: AmTest Air Quality, Inc., 1994b; 1994c.

TABLE 4.4.1-12. PAH EMISSION FACTORS FOR PRIMARY ALUMINUM  
PRODUCTION: CASTING OPERATIONS<sup>a</sup>

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>b</sup>	Emission Factor Rating
3-03-001-99	EPC Casting Operations <sup>c</sup>	None	Benz(a)anthracene	4.40E-05 (2.20E-05)	E
			Benzo(a)pyrene	1.22E-04 (6.10E-05)	E
			Benzo(b)fluoranthene	1.38E-04 (6.90E-05)	E
			Benzo(k)fluoranthene	4.20E-05 (2.10E-05)	E
			Chrysene	1.80E-05 (9.00E-06)	E
			Anthracene	4.80E-04 (2.40E-04)	E
			Benzo(ghi)perylene	6.20E-05 (3.10E-05)	E
			Fluoranthene	3.00E-05 (1.50E-05)	E
			Benzo(e)pyrene	6.80E-05 (3.40E-05)	E

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(continued)

TABLE 4.4.1-12. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>b</sup>	Emission Factor Rating
3-03-001-99	Green Sand Casting Operation	None	Anthracene	3.20E-04 (1.60E-04)	E
			Fluorene	4.60E-04 (2.30E-04)	E
			Naphthalene	1.14E-02 (5.70E-03)	E

<sup>a</sup>Emissions from pouring, cooling, and shakeout of aluminum castings.

<sup>b</sup>Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of aluminum cast.

<sup>c</sup>Evaporative pattern casting process (lost foam process).

Source: Gressel et al., 1988.



TABLE 4.4.1-13. PRIMARY ALUMINUM PRODUCTION FACILITIES  
IN THE UNITED STATES IN 1992

Facility	Location
Alcan Aluminum Corporation	Sebree, KY
Alumax, Inc.	Mount Holly, SC Frederick, MD Ferndale, WA
Aluminum Company of America	Alcoa, TN Badin, NC Evansville, IN Massena, NY Rockdale, TX Wenatchee, WA
Columbia Aluminum Corporation	Goldendale, WA
Columbia Falls Aluminum Company	Columbia Falls, MT
Kaiser Aluminum and Chemical Corporation	Mead, WA Tacoma, WA
National-Southwire Aluminum Company	Hawesville, KY
Noranda Aluminum, Inc.	New Madrid, MO
Northwest Aluminum Corporation	The Dalles, OR
Ormet Corporation	Hannibal, OH
Ravenswood Aluminum Corporation	Ravenswood, WV
Reynolds Metals Company	Longview, WA Massena, NY Troutdale, OR
Vanalco Inc.	Vancouver, WA

NOTE: This list is subject to change as market conditions and facility ownership changes, plants are closed down, etc. The reader should verify the existence of specific facilities by consulting current lists and/or the plants themselves. The level of POM emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

Source: Plunkert and Sehnke, 1993.

#### SECTION 4.4.1 REFERENCES

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#### 4.4.2 Sintering in the Iron and Steel Industry

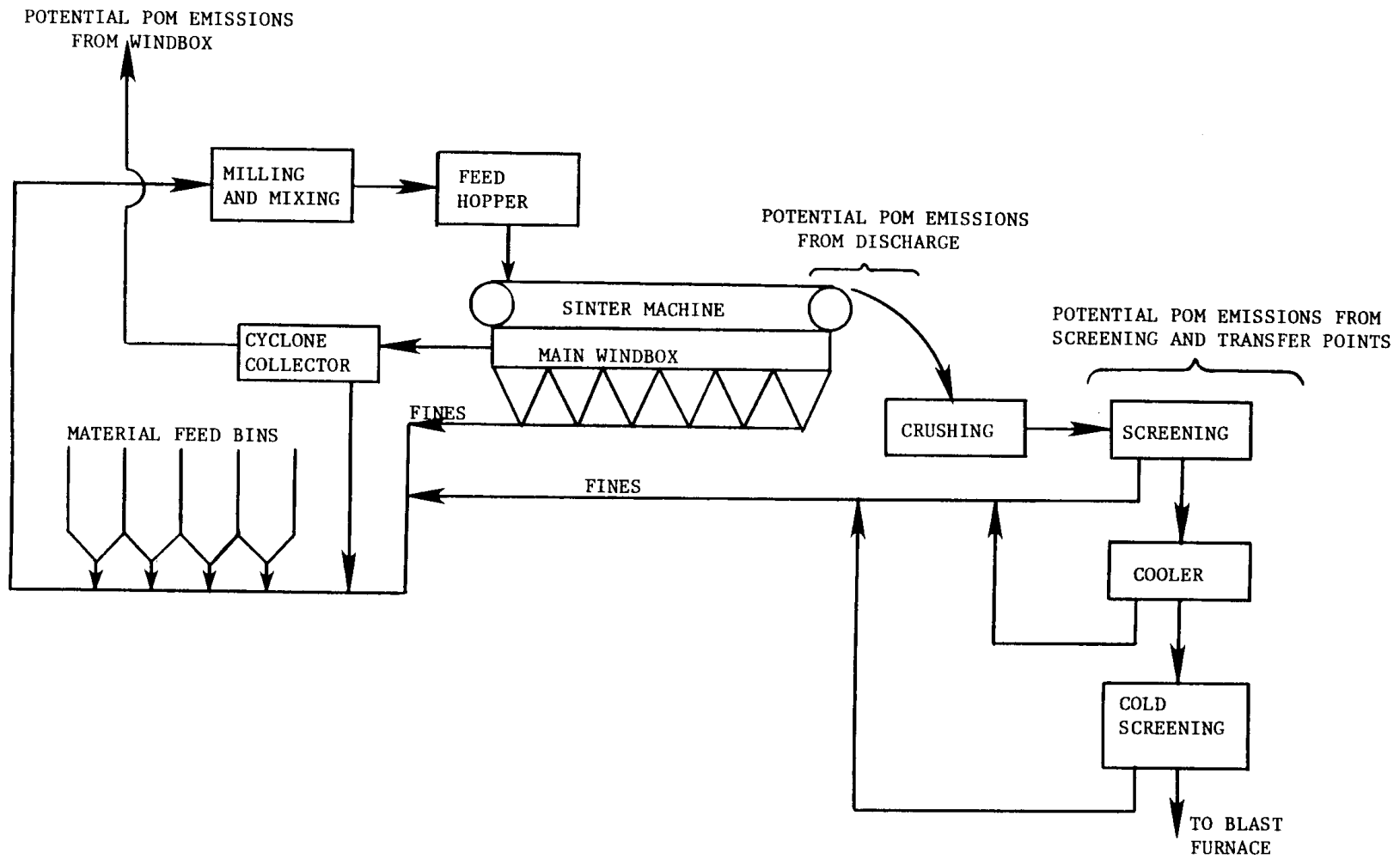
##### Process Description

In the iron and steel industry, the sintering process converts materials such as fine iron ore concentrates, blast furnace flue dust, mill scale, turnings, coke fines, and limestone fines into an agglomerated product that is suitable for use as blast furnace feed material. Sintering is necessary to prevent fine iron ore material (whether in natural or concentrated ores) from being blown out of the top of a blast furnace (Kelly, 1983; U.S. EPA, 1981). A typical sintering operation is illustrated in Figure 4.4.2-1.

Sintering begins with mixing iron-bearing materials with coke or coal fines, limestone fines (a flux material), water, and other recycled dusts (e.g., blast furnace flue dust) to obtain the desired sinter feed composition. The prepared feed is distributed evenly onto one end of a continuous traveling grate or strand. After the feed has been deposited on the strand, the coke on the mixture is ignited by a gas- or oil-fired furnace. After the coke has been ignited, the traveling strand passes over windboxes, where an induced downdraft maintains combustion in the sinter bed. This combustion creates sufficient temperatures (2,400 to 2,700°F [1,300 to 1,500°C]) to fuse the metal particles into a porous clinker that can be used as blast furnace feed (Kelly, 1983; U.S. EPA, 1981). Approximately 2.5 tons of raw materials, including water and fuel, are required to produce one ton of product sinter (U.S. EPA, 1995).

After the sintering process is completed, the sintered material is discharged from the sinter strand into a crushing operation. Following crushing, the broken sinter falls onto sizing screens, where undersize material is collected and recycled to the start of the sintering process. The oversize sinter clinker is then sent to a cooling process. The most common types of sinter coolers include circular or straight-line moving beds, quiescent beds, or shafts. Air or water is used as the cooling medium in these coolers, with air being prevalent in newer plants and water being dominant in older plants. The cooled sinter is either sent directly to a blast furnace, sent to storage, or screened again prior to blast furnace usage to obtain a more precise size specification (Kelly, 1983; U.S. EPA, 1981).

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Figure 4.4.2-1. Configuration of a Typical Sintering Facility

Source: U.S. EPA , 1977.

POM emissions originate in the sintering process from the burning of coke and potentially oily materials in the sinter feed. POM emissions may be released from the sinter machine windbox, the sinter machine discharge point, and the sinter product processing operations (i.e., crushing, screening, and cooling). Because of the high temperatures used in sintering operations, it is probable that sinter plant POM emissions are in both gaseous and particulate forms (Kelly, 1983; Siebert et al., 1978).

Emissions control at sintering facilities typically involves emissions collection and conveyance to a standard particulate control device such as a baghouse, ESP, or wet scrubber. If substantial quantities of POM emissions are in gaseous form, wet scrubbers would likely be most efficient in reducing total POM because gaseous compounds would be condensed in the scrubber (Kelly, 1983; U.S. EPA, 1981; U.S. EPA, 1977; Siebert et al., 1978).

#### Emission Factors

Emission factor data for PAHs from sintering operations were not available at the time this report was prepared. The only available information reported an emission factor for benzo(a)pyrene (BaP) in the range of  $1.2 \times 10^6$  to  $2.2 \times 10^{-3}$  lb/ton (600  $\mu\text{g}/\text{Mg}$  to 1.1 g/Mg) of sinter feed processed. The precise source of the emissions (windbox, discharge point, etc.) and the control status of the source are not defined in the literature. Available data did not indicate whether the range of emission factors represented only particulate BaP or particulate and gaseous BaP emissions (Siebert et al., 1978). Therefore, this emission factor should be applied with caution, recognizing the uncertainty in its development and low confidence in its quality.

#### Source Locations

Iron and steel sintering facilities are located in conjunction with the operation of iron and steel blast furnaces. According to EPA, there were 11 integrated iron and steel manufacturing facilities in the United States with sintering operations in 1993 (Mulrine Telecon, 1994). The names and locations of these facilities are listed in Table 4.4.2-1.

TABLE 4.4.2-1. LOCATIONS OF IRON AND STEEL INDUSTRY  
SINTER PLANTS IN 1993

Company	Plant Location
Arnco Steel	Ashland, KY
Arnco Steel	Middletown, OH
Bethlehem Steel	Burns Harbor, IN
Bethlehem Steel	Sparrows Point, MD
Geneva Steel	Orem, UT
Inland Steel	East Chicago, IN
LTV Steel	East Chicago, IN
USX	Gary, IN
NCI Steel	Youngstown, OH
Weirton Steel	Weirton, WV
Wheeling-Pittsburgh	Steubenville, OH

NOTE: This list is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current list and/or the plants themselves.

Source: Mulrine Telecon, 1994.

## SECTION 4.4.2 REFERENCES

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Siebert, P.C. et al. Preliminary Assessment of the Sources, Control and Population Exposure to Airborne Polycyclic Organic Matter (POM) as Indicated by Benzo(a)pyrene (BaP). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Pollutant Strategies Branch, Research Triangle Park, North Carolina. Prepared under EPA Contract No. 68-02-2836. pp. 78-79. 1978.

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#### 4.4.3 Ferroalloy Manufacturing

##### Process Description

Ferroalloys are crude alloys of iron and one or more other elements that are used for deoxidizing molten steels and making alloy steels. The major types of ferroalloys produced are (Houck, 1993):

Ferroaluminum	Ferrosilicon
Ferroboron	Ferrotitanium
Ferrocolumbium	Ferrovandium
Ferrochromium	Ferrotungsten
Ferrochromium-silicon	Ferrozirconium
Ferromanganese	Manganese metal
Ferromolybdenum	Nickelcolumbium
Ferronickel	Silicon metal
Ferrophosphorus	Silicomanganese

Ferroalloys can be produced by five different processes; the primary method uses electric arc furnaces (EAFs). Ferroalloy manufacturing is a potential source of emissions of POM compounds because coke or coal is charged to the high-temperature smelting furnaces used in the ferroalloy industry and burned. Because combustion efficiency in the furnace environment is low, unburned hydrocarbons, including PAHs, are formed and emitted with the furnace exhaust. However, ferroalloy production processes other than EAFs have not been identified as POM emission sources (Kelly, 1983).

The EAF method of ferroalloy production is depicted in Figure 4.4.3-1 (U.S. EPA, 1980; U.S. EPA, 1974). Metal ores and other necessary raw materials such as quartz or quartzite (slagging materials), alumina (a reducing agent), limestone, coke or coal, and steel scrap are brought to ferroalloy facilities by ship, truck, or rail and stored on site. Depending on its moisture content and physical configuration, metal ore may need to be dried and/or sintered

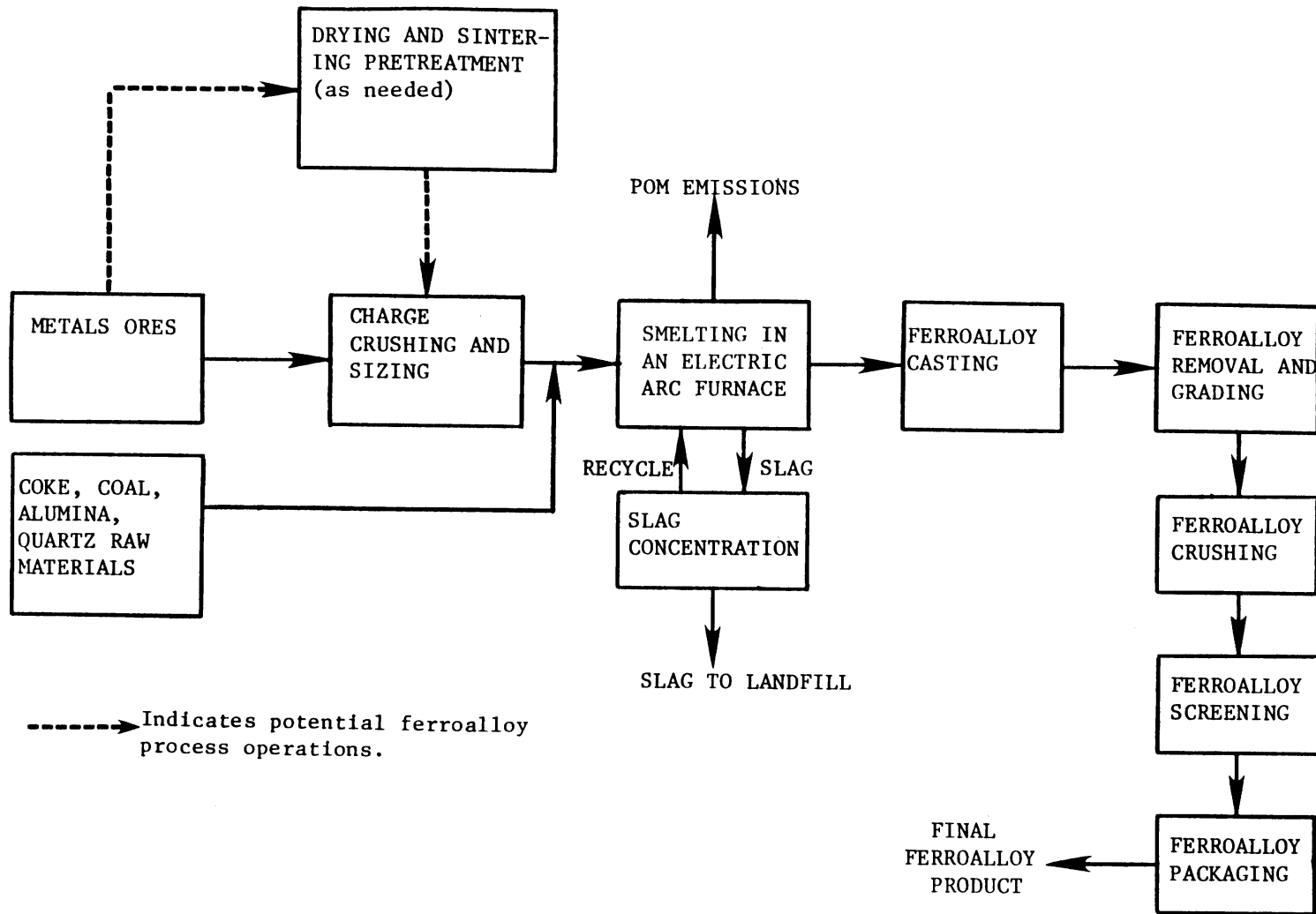


Figure 4.4.3-1. Typical Electric Arc Furnace Ferroalloy Manufacturing Process

Source: U.S. EPA, 1980

prior to being crushed, sized, and mixed with other process raw materials. After the proper charge mixture has been prepared, the charge is weighed and fed to a submerged EAF for smelting.

Three types of EAFs can be used for ferroalloy production: open, semi-covered, and covered (sealed). They may be charged continuously or intermittently. EAFs contain three carbon electrodes, which are vertically suspended above the furnace hearth and extend 3 to 5 feet (1 to 1.5 m) into the charge materials. Three-phase current arcs through the charge materials from electrode to electrode, and the charge is smelted as electrical energy is converted to heat. The intense heat around the electrodes (4,000 to 5,000°F [2,204 to 2,760°C]) results in carbon reduction of the metal (e.g., chrome, manganese) and iron oxides in the charge and the formation of the particular ferroalloy. EAF capacities range from 0.25 to 65 tons (0.23 to 59 Mg). Melting capacities range up to 10 Mg (11 tons) per hour (Barnard, 1990). Nine to 11 pounds of carbon electrode are consumed per ton of metal melted (U.S. EPA, 1990).

The molten ferroalloy is periodically tapped into ladles from tapholes in the lower furnace wall, cast into molds, and allowed to cool and solidify. The casts are then removed from the molds and graded and broken. The broken ferroalloy is passed through a crusher and screened. The ferroalloy product is then stored, packaged, and shipped to the consumer.

Impurities from the smelting process are trapped in a slag that forms inside the EAF. The slag is periodically tapped and treated by a concentration process to recovery metal values. Slag is processed in a flotation system, where metal particles sink to the bottom while the slag floats. The recovered metals are recycled to the furnace and the remaining slag is removed and disposed of.

Open EAF--Of the three types of EAFs that may be used to produce ferroalloys, open furnaces are the most common type and also have the highest potential for particulate emissions (U.S. EPA, 1974). An open EAF is pictured in Figure 4.4.3-2. A hood is usually located 6 to 8 feet (1.8 to 2.4 m) above the furnace crucible rim. Dust and fumes from the smelting process

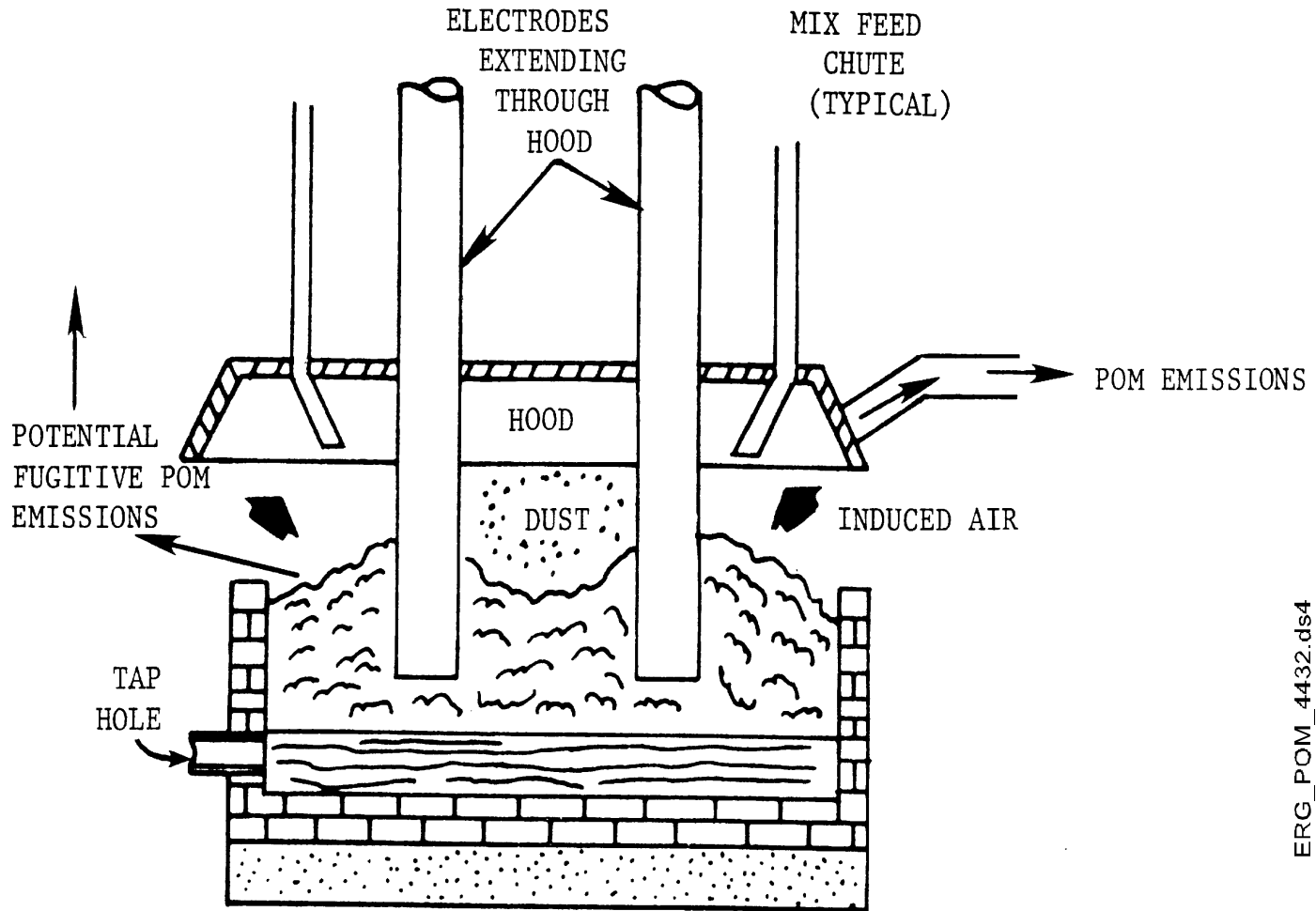


Figure 4.4.3-2. Open Electric Arc Furnace

are drawn into the hood along with large volumes of ambient air. Advantages of the open furnace include the ability to stoke it during operation and the flexibility to manufacture several types of ferroalloy without altering the furnace design.

Semi-covered EAF--A semi-covered EAF is pictured in Figure 4.4.3-3. A cover seals the top of the furnace except for openings around the electrodes through which raw material is charged. These furnaces are either hooded or maintained under negative pressure to collect emissions from around the electrodes. Because semi-covered furnaces cannot be stoked, crusting and bridging of ferroalloys around the electrodes and charge holes may prevent uniform descent of the charge into the furnace and blows (jets of extremely hot gases originating in the high-temperature zone near the electrode tips) may emerge around the electrodes at high velocity (U.S. EPA, 1980; U.S. EPA, 1974; U.S. EPA, 1984).

Sealed EAF--The third type of EAF, the closed or sealed furnace, is illustrated in Figure 4.4.3-4. Packing is used to seal the cover around the electrodes and charging chutes. The furnace is not stoked, and a slight positive pressure is maintained to prevent leakage of the air into the furnace. Care must also be taken to prevent water leaks, which could cause an explosive gas release that could damage the furnace and threaten worker safety. Sealed furnace designs are specifically used in the manufacture of narrow families of ferroalloys, so plants using sealed furnaces have less flexibility to produce different types of ferroalloys.

Emissions Control Techniques--All types of EAFs produce emissions consisting of a variety of compounds, including POM, in both gaseous and particulate forms. Baghouses were used to control emissions from 87 percent of the open ferroalloy furnaces operating in 1980. Testing of these control systems indicates total PM removal efficiency of over 99 percent. Such systems are also effective in controlling POM compounds adsorbed onto PM<sub>10</sub> emissions. Testing conducted on baghouses controlling open furnace emissions indicates organic matter control efficiencies from 25 to 65 percent, with benzo(a)pyrene (BaP) control efficiencies of 61 to 74 percent. Higher organic matter control efficiencies were achieved by baghouses controlling open furnace emissions than by those controlling secondary fume emissions from semi-covered EAFs (Westbrook, 1983).

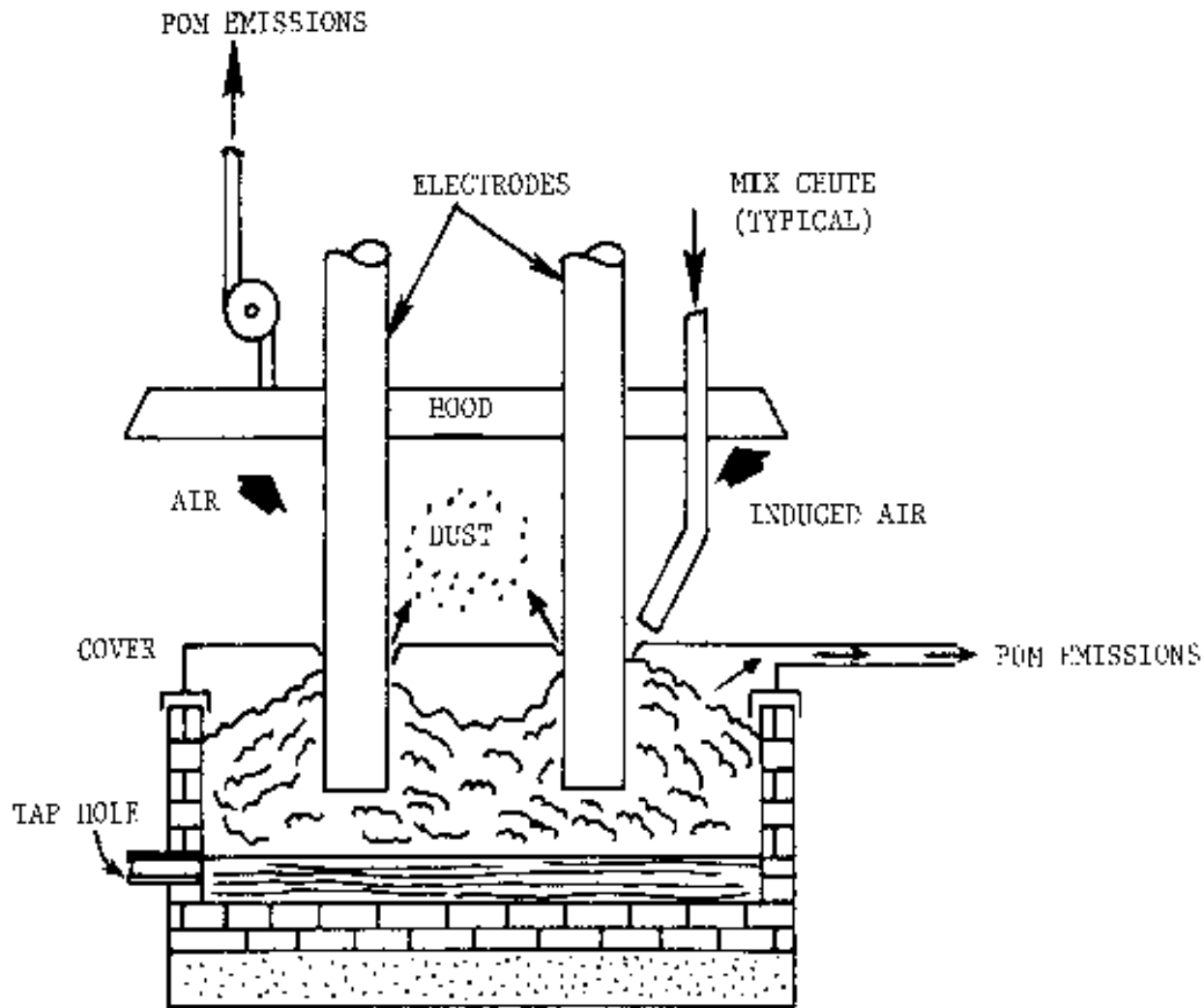


Figure 4.4.3-3. Semi-covered Electric Arc Furnace

Source: U.S. EPA, 1974

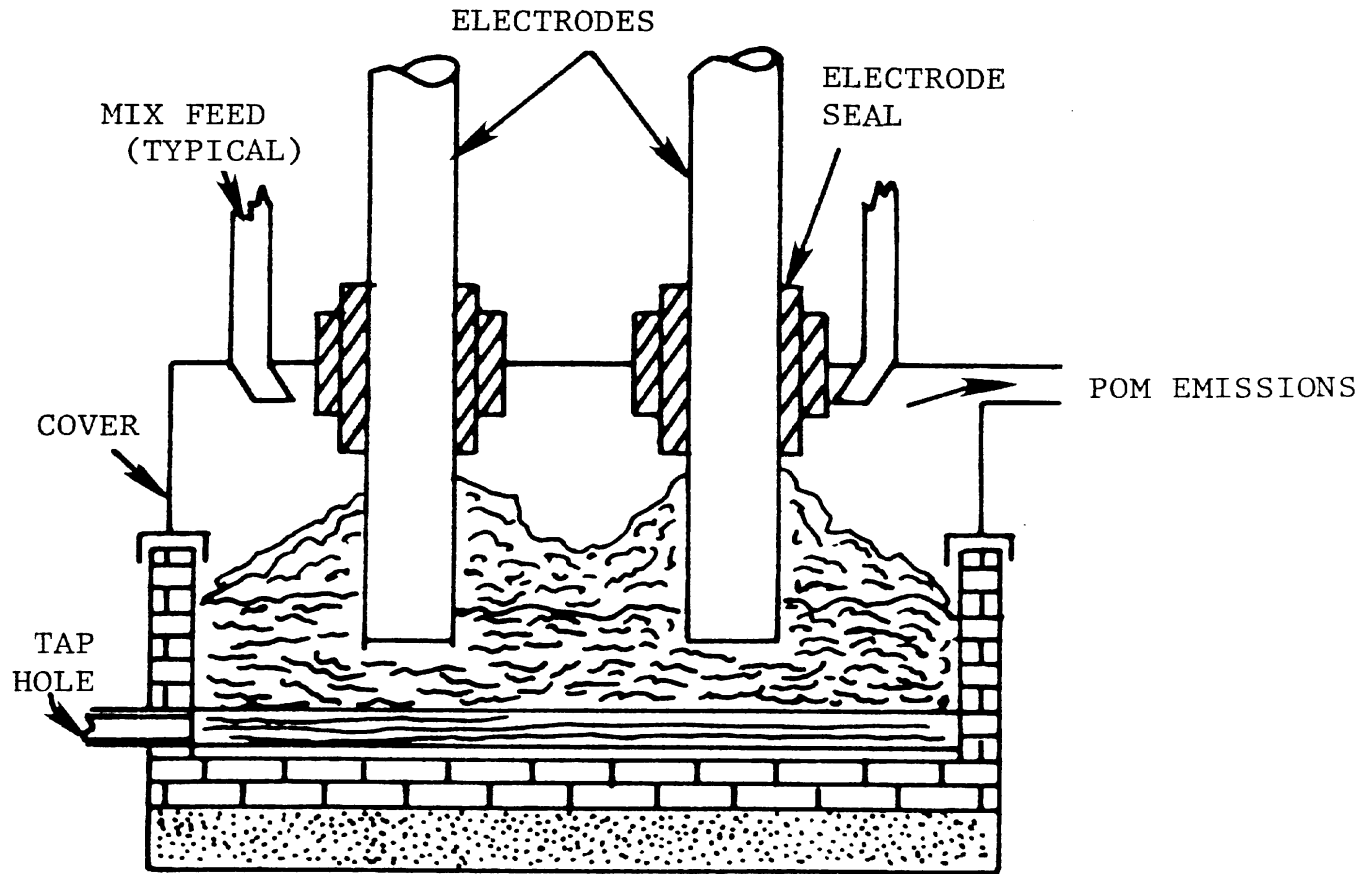


Figure 4.3.3-4. Covered (Sealed) Electric Arc Furnace

Source: U.S. EPA, 1974

High-pressure-drop venturi scrubbers and ESPs have also been applied to open ferroalloy EAFs. Reported total PM collection efficiencies for scrubbers ranged from 94 to 98 percent. When ESPs were used, the gas was conditioned with ammonia to enhance particulate resistivity and increase collection efficiency. Estimated total PM removal efficiencies for the ESPs were 98 percent (Kelly, 1983; U.S. EPA, 1980; U.S. EPA, 1974; U.S. EPA, 1984).

Uncontrolled organic matter generation rates of open EAFs are generally lower than those of covered furnaces on a throughput basis because of more complete combustion of gases. However, organic matter emissions to the atmosphere may be as high or higher from an open furnace controlled by a baghouse than from a sealed furnace producing an equivalent product controlled by a scrubber (Westbrook, 1983).

In the case of semi-covered furnaces, offgases are drawn from beneath the furnace cover through ducts leading to a control device. However, fugitive particulates and fumes escape through the openings around the electrodes. Generally, hoods are in place above the furnaces to capture these emissions along with tapping fumes and route them to a secondary fume control device such as a baghouse. One test report indicated a control efficiency for organic matter for a semi-covered furnace secondary fume baghouse of 13 percent (Westbrook, 1983). Wet scrubbers, including both multistage centrifugal scrubbers and venturi scrubbers, are also used on semi-covered ferroalloy furnaces. Up to 99 percent total PM removal efficiency has been reported for centrifugal scrubbers. Venturi units can exhibit even greater PM efficiencies. Reported control efficiencies for organic matter from scrubber-controlled semi-covered EAFs range from 64 to 88 percent, with BaP control efficiencies reported at greater than 99 percent (Westbrook, 1983).

Venturi scrubbers are commonly used to control emissions from sealed ferroalloy EAFs; however, a few installations use baghouses. In general, total uncontrolled emissions vented to a control device from a sealed furnace are lower than emissions from other ferroalloy EAFs because no air enters sealed furnaces. Resultant gas flows (volumes) to the control device are only 2 to 5 percent of those from open furnaces (U.S. EPA, 1980). However, uncontrolled organic matter in sealed and semi-covered EAFs with minimal undercover combustion may be



significantly higher than generation in semi-covered EAFs with undercover combustion or open furnaces (Westbrook, 1983).

### Emission Factors

PAH emission factor data were identified for open, semi-covered, and sealed ferroalloy manufacturing EAFs in two test reports (U.S. EPA, 1980; Westbrook, 1983). Emission factors are presented in Tables 4.4.3-1 to 4.4.3-4. All emission factor units are in lb/MMBtu (g/MW-h) of energy consumed by the furnace. The average amount of energy consumed in EAF operation per unit output is approximately 21.85 MMBtu/ton (7.05 MW-hr/Mg) of alloy produced (Chin Telecon, 1994).

PAH emission factors for open EAFs producing silicon metal are listed in Table 4.4.3-1. The emission factors are based on test data from a single EAF with a rated power capacity of 58 MMBtu/hr (17 MW). Furnace emissions were controlled by a baghouse and sampling for PAHs was conducted at the outlet of the baghouse. BaP emissions were quantified both before and after the baghouse (uncontrolled and controlled). The baghouse control efficiency for BaP was estimated at 61.1 percent. Sampling and analytical methods were used to quantify both particulate and vapor phase PAHs (Westbrook, 1983).

PAH emission factors for semi-covered EAFs producing 50 percent ferrosilicon are presented in Table 4.4.3-2. The emission factors are based on test data from two wet scrubber controlled EAFs. Both test programs utilized sampling and analytical methods capable of quantifying both particulate and vapor phase POM. Westbrook (1983) measured pre-scrubber (uncontrolled) BaP emissions from a 147 MMBtu/hr (43 MW) EAF of  $2.62\text{E-}13$  lb/MMBtu (4.06 g/MW-h). Controlled BaP emissions from the same unit were estimated at  $1.55\text{E-}5$  lb/MMBtu (0.024 g/MW-h), assuming the scrubber flare was not operating and 73.6 percent capture of BaP in the secondary fume baghouse. Scrubber controlled BaP emissions reported by EPA (1980) for a 57 MMBtu/hr (16.8 MW) EAF producing 50 percent ferrosilicon were substantially higher, at  $6.46\text{E-}4$  lb/MMBtu (1.0 g/MW-h). All additional PAH emission

factors reported in Table 4.4.3-2 represent scrubber controlled emissions as reported by EPA (1980). Total POM emissions were estimated to be 0.088 lb/MMBtu (137 g/MW-h).

PAH emission factors for covered EAFs are presented in Tables 4.4.3-3 and 4.4.3-4. The emission factors are based on test data from a single furnace operating under two different ferroalloy and control scenarios. Both particulate and vapor phase PAHs were quantified in the test program (U.S. EPA, 1980).

The emission factors in Table 4.4.3-3 represent uncontrolled PAH emissions from the closed EAF during the production of ferromanganese. Sampling during this furnace operating scenario was conducted prior to the wet scrubber and flare control system. The furnace operating power during testing was 59.1 MMBtu/hr (17.3 MW). Total uncontrolled POM emissions were estimated to be 0.101 lb/MMBtu (156 g/MW-h).

The emission factors in Table 4.4.3-4 represent scrubber controlled emissions from the same closed EAF during the production of silicomanganese. During this test series, samples were taken after the high-pressure-drop wet scrubber and prior to the flare. The furnace operating power during testing under silicomanganese production was 76.8 MMBtu/hr (22.5 MW). Controlled total POM emissions were estimated to be 6.46 E-4 lb/MMBtu (1.0 g/MW-h) (U.S. EPA, 1980).

#### Source Locations

The latest information published by the U.S. Bureau of Mines on the locations of ferroalloy manufacturing facilities in the United States is listed in Table 4.4.3-5. According to these data, as of 1992, 27 companies operated a total of 34 ferroalloy facilities in the United States. Ohio and Pennsylvania contained the greatest number of ferroalloy production facilities, with five and six facilities, respectively. Ohio, Pennsylvania, New York, and Alabama together contained approximately 50 percent of the total number of facilities nationwide (Houck, 1993).

TABLE 4.4.3-1. PAH EMISSION FACTORS FOR OPEN ELECTRIC ARC FURNACES PRODUCING SILICON METAL

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MW-h) <sup>a</sup>	Emission Factor Range	Emission Factor Rating
3-03-006-04	Electric Arc Furnace	None	Benzo(a)pyrene	1.36E-05 (0.021)	---	E
3-03-006-04	Electric Arc Furnace	Baghouse	Benz(a)anthracene	7.42E-05 (0.115)	---	E
			Benzo(a)pyrene	5.17E-06 (8.00E-03)	ND - 1.55E-4 (ND - 0.240)	E
			Chrysene	2.60E-04 (0.402)	---	E
			Anthracene	4.19E-03 (6.49)	---	E
			Fluoranthene	1.60E-03 (2.47)	---	E
			Fluorene	3.45E-04 (0.534)	---	E
			Naphthalene	2.33E-02 (36.1)	---	E
			Pyrene	8.91E-04 (1.38)	---	E
			Methylanthracenes	1.22E-03 (1.90)	---	E
	Phenylanthracene	1.00E-03 (1.55)	---	E		

<sup>a</sup>Emission factors are in lb (g) of pollutant emitted per MMBtu (kw-h).

Source: Westbrook, 1983.

TABLE 4.4.3-2. PAH EMISSION FACTORS FOR SEMI-COVERED ELECTRIC ARC FURNACES  
PRODUCING 50 PERCENT FERROSILICON

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MW-h) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MW-h) <sup>a</sup>	Emission Factor Rating	Reference
3-04-006-01	Electric Arc Furnace	None	Benzo(a)pyrene	2.62E-03 (4.06)	---	E	Westbrook, 1983
3-04-006-01	Electric Arc Furnace	Wet Scrubber	Benz(a)anthracene	4.13E-03 (6.40)	---	E	U.S. EPA, 1980
			Benzo(a)pyrene	3.31E-04 (0.512)	1.55E-05 - 6.46E-04 (0.024 - 1.00)	E	Westbrook, 1983; U.S. EPA, 1980
			Benzo(b)fluoranthene	1.36E-03 (2.10)	---	E	U.S. EPA, 1980
			Benzo(k)fluoranthene	6.46E-05 (0.100)	---	E	U.S. EPA, 1980
			Chrysene	3.16E-03 (4.90)	---	E	U.S. EPA, 1980
			Indeno(1,2,3-cd)pyrene	4.33E-04 (0.670)	---	E	U.S. EPA, 1980
			Anthracene	7.23E-03 (11.2)	---	E	U.S. EPA, 1980
			Benzo(ghi)perylene	1.23E-03 (1.90)	---	E	U.S. EPA, 1980
			Fluoranthene	1.08E-02 (16.7)	---	E	U.S. EPA, 1980
			Fluorene	2.96E-02 (45.9)	---	E	U.S. EPA, 1980
			Phenanthrene	7.23E-03 (11.2)	---	E	U.S. EPA, 1980

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(continued)

TABLE 4.4.3-2. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MW-h) <sup>a</sup>	Emission Factor Range in lb/MMBtu (g/MW-h) <sup>a</sup>	Emission Factor Rating	Reference
3-04-006-01 (continued)	Electric Arc Furnace (continued)	Wet Scrubber (continued)	Pyrene	1.12E-02 (17.4)	---	E	U.S. EPA, 1980
			Anthanthrene	3.29E-04 (0.510)	---	E	U.S. EPA, 1980
			Benzo(a) and Benzo(b)fluorene	4.84E-04 (0.750)	---	E	U.S. EPA, 1980
			Benzo(e)pyrene	3.16E-04 (0.490)	---	E	U.S. EPA, 1980
			Benzo(ghi)fluoranthene	3.49E-03 (5.40)	---	E	U.S. EPA, 1980
			Coronene	3.94E-04 (0.610)	---	E	U.S. EPA, 1980
			Cyclopenta(def)-phenanthrene	4.20E-03 (6.50)	---	E	U.S. EPA, 1980
			Methylanthracenes	5.94E-04 (0.920)	---	E	U.S. EPA, 1980
			Methylpyrene	2.58E-05 (0.0400)	---	E	U.S. EPA, 1980
			Perylene	1.68E-04 (0.260)	---	E	U.S. EPA, 1980

<sup>a</sup>Emission factors are in lb (g) of pollutant emitted per MMBtu (MW-h).

TABLE 4.4.3-3. PAH EMISSION FACTORS FOR COVERED ELECTRIC ARC FURNACES  
PRODUCING FERROMANGANESE

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MW-h) <sup>a</sup>	Emission Factor Rating
3-03-006-51	Electric Arc Furnace	None	Chrysene	7.75E-03 (12.0)	E
			Dibenz(a,h)anthracene	1.42E-04 (0.220)	E
			Indeno(1,2,3-cd)pyrene	9.69E-04 (1.50)	E
			Anthracene	3.54E-02 (54.9)	E
			Benzo(ghi)perylene	2.26E-04 (0.350)	E
			Fluoranthene	3.54E-02 (54.9)	E
			Fluorene	2.58E-03 (4.00)	E
			Pyrene	3.68E-04 (0.570)	E
			Benzo(e)pyrene	8.39E-03 (13.0)	E
			Carbazole	1.55E-03 (2.40)	E
			Coronene	8.39E-05 (0.130)	E
Methylanthracenes	3.67E-03 (6.00)	E			

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(continued)

TABLE 4.4.3-3. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MW-h) <sup>a</sup>	Emission Factor Rating
3-03-006-51 (continued)	Electric Arc Furnace (continued)	None	Methylchrysenes	8.39E-04 (1.30)	E
			Methylpyrene	2.26E-03 (3.50)	E
			Perylene	4.97E-04 (0.770)	E
			7,12-Dimethylbenz(a)anthracene	9.04E-05 (0.140)	E
			Methylbenzopyrenes	1.94E-04 (0.300)	E
			3-Methylcholanthrene	6.46E-05 (0.100)	E
			Dibenzo(c,g)carbazole	1.29E-05 (0.0200)	E
			Dibenzo(ai+ah)pyrenes	8.39E-05 (0.130)	E

<sup>a</sup>Emission factors are in lb (g) of pollutant emitted per MMBtu (MW-h).

Source: U.S. EPA, 1980.

TABLE 4.4.3-4. PAH EMISSION FACTORS FOR COVERED ELECTRIC ARC FURNACES  
PRODUCING SILICOMANGANESE

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MW-h) <sup>a</sup>	Emission Factor Rating
3-03-006-54	Electric Arc Furnace	Wet Scrubber	Chrysene	2.62E-06 (3.90)	E
			Anthracene	3.29E-04 (0.510)	E
			Fluoranthene	3.47E-05 (0.0580)	E
			Fluorene	2.32E-04 (0.360)	E
			Pyrene	3.42E-05 (0.0530)	E
			Methylanthracenes	1.10E-05 (0.0170)	E
			Methylpyrene	7.75E-07 (1.20E-03)	E

<sup>a</sup>Emission factors are in lb (g) of pollutant emitted per MMBtu (MW-h).

Source: U.S. EPA, 1980.



TABLE 4.4.3-5. LOCATIONS OF FERROALLOY PRODUCERS  
IN THE UNITED STATES IN 1992

Producer	Plant Location	Type of Furnace
<u>Ferroalloys</u>		
AMAX Inc., Climax Molybdenum Company Division	Langeloth, PA	Metallothermic
America Alloys, Inc.	New Haven, WV	Electric Arc
Applied Industrial Minerals Corporation (AIMCOR)	Bridgeport, AL	Electric Arc
Bear Metallurgical, Inc.	Butler, PA	Metallothermic
Cabot Corporation	Revere, PA	Metallothermic
Cyprus Minerals Company	Greenvalley, AZ	Metallothermic
Dow Corning Corporation	Springfield, OR	Electric Arc
Elkem A/S, Elkem Metals Company	Alloy, WV Ashtabula, OH Marietta, OH Niagara Falls, NY	Electric Arc and Electrolytic
Galt Alloys, Inc.	Canton, OH	Electric Arc
Glenbrook Nickel Company	Riddle, OR	Electric Arc
Globe Metallurgical, Inc.	Beverly, OH Selma, AL	Electric Arc
HTP Company	Sharon, PA	Metallothermic
Keokuk Ferro-Sil, Inc.	Keokuk, IA	Electric Arc
Kerr-McGee Chemical Corporation	Hamilton, MS	Electrolytic
Macalloy, Inc.	Charleston, SC	Electric Arc
Metallurg, Inc., Shieldalloy	Cambridge, OH	Electric Arc
Metallurgical Corporation	Newfield, NJ	Metallothermic
Reading Alloys, Inc.	Robesonia, PA	Metallothermic
Satra Concentrates, Inc.	Steubenville, OH	Slag conversion
Silicon Metaltech, Inc.	Wenatchee, WA	Electric Arc

TABLE 4.4.3-5. (Continued)

Producer	Plant Location	Type of Furnace
Simetco	Montgomery, AL	Electric Arc
SKW Alloys, Inc.	Calvert City, KY Niagara Falls, NY	Electric Arc
Strategic Minerals Corporation (STRATCOR)	Niagara Falls, NY	Electric Arc
Teledyne, Inc., Teledyne Wah Chang, Albany Division	Albany, OR	Metallothermic
Union Oil Company of California, Molycorp, Inc.	Washington, PA	Electric Arc and Metallothermic
<u>Ferrophosphorus</u>		
FMC Corporation, Industrial Chemical Division	Pocatello, ID	Electric Arc and metallothermic
Monsanto Company, Monsanto Industrial Chemicals Company	Columbia, TN Soda Springs, ID	Electric Arc and metallothermic
Occidental Petroleum Corporation	Columbia, TN	Electric Arc and metallothermic

NOTE: This list is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of specific facilities by consulting current lists and/or the plants themselves. The level of PAH emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

Source: Houck, 1993.

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#### 4.4.4 Iron and Steel Foundries

##### Process Description

Iron and steel foundries can be defined as those that produce gray, white, ductile, or malleable iron and steel castings. Both cast irons and steels are solid solutions of iron, carbon, and various alloying materials. Although there are many types of each, the iron and steel families can be distinguished by their carbon content. Cast irons typically contain 2 percent carbon or greater; cast steels usually contain less than 2 percent carbon (U.S. EPA, 1980).

Iron castings are used in almost all types of equipment, including motor vehicles, farm machinery, construction machinery, petroleum industry equipment, electrical motors, and iron and steel industry equipment.

Steel castings are used in motor vehicles, railroad equipment, construction machinery, aircraft, agricultural equipment, ore refining machinery, and chemical manufacturing equipment (U.S. EPA, 1980). Steel castings are classified on the basis of their composition and heat treatment, which determine their end use. Classifications include carbon, low-alloy, general-purpose-structural, heat-resistant, corrosion-resistant, and wear-resistant.

The following four basic operations are performed in all iron and steel foundries:

- Storage and handling of raw materials;
- Melting of the raw materials;
- Transfer of the hot molten metal into molds; and
- Preparation of the molds to hold the molten metal.

Other processes present in most, but not all, foundries include:

- Sand preparation and handling;
- Mold cooling and shakeout;
- Casting cleaning, heat treating, and finishing;
- Coremaking; and
- Pattern making.

A generic process flow diagram for iron and steel foundries is shown in Figure 4.4.4-1. Figure 4.4.4-2 depicts the emission points in a typical iron foundry (U.S. EPA, 1995).

Iron and steel castings are produced in a foundry by injecting or pouring molten metal into cavities of a mold made of sand, metal, or ceramic material. Input metal is melted by the use of a cupola (a cylindrical shell with either a refractory-lined or water-cooled inner wall), an electric arc furnace (EAF), or an induction furnace. About 70 percent of all iron castings are produced using cupolas, with lesser amounts produced in EAFs and induction furnaces. However, the use of EAFs in iron foundries is increasing. Steel foundries rely almost exclusively on EAFs or induction furnaces for melting purposes.

In either type of foundry, when the poured metal has solidified, the molds are separated and the castings removed from the mold flasks on a casting shakeout unit. Abrasive (shotblasting) cleaning, grinding, and heat treating are performed as necessary. The castings are then inspected and shipped to another industry for machining and/or assembly into a final product (U.S. EPA, 1980).

In a typical foundry operation, charges to the melting unit are sorted by size and density and cleaned (as required) prior to being put into the melter. Charges consist of scrap metal, ingot, carbon (coke), and flux. Prepared charge materials are placed in crane buckets, weighed,

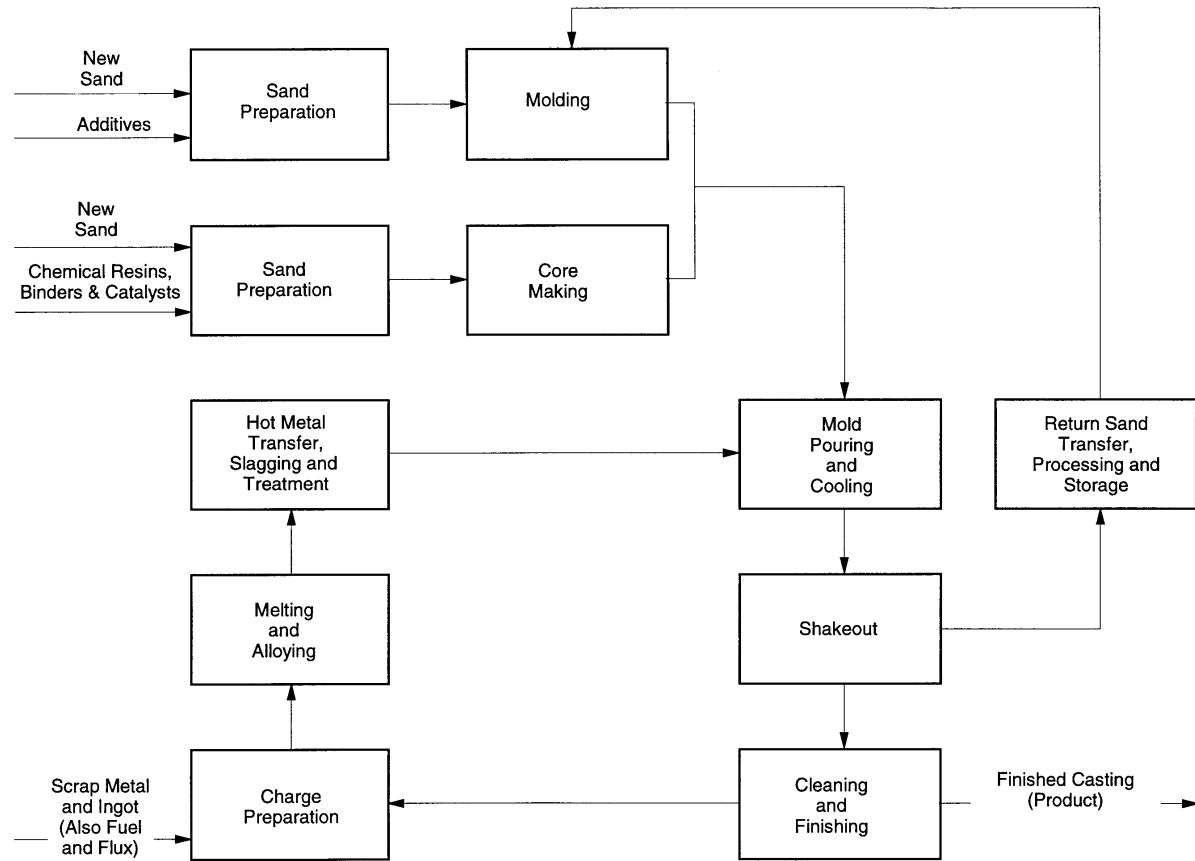


Figure 4.4.4-1. Process Flow Diagram for a Typical Sand-cast Iron and Steel Foundry

Source: U.S. EPA, 1980.

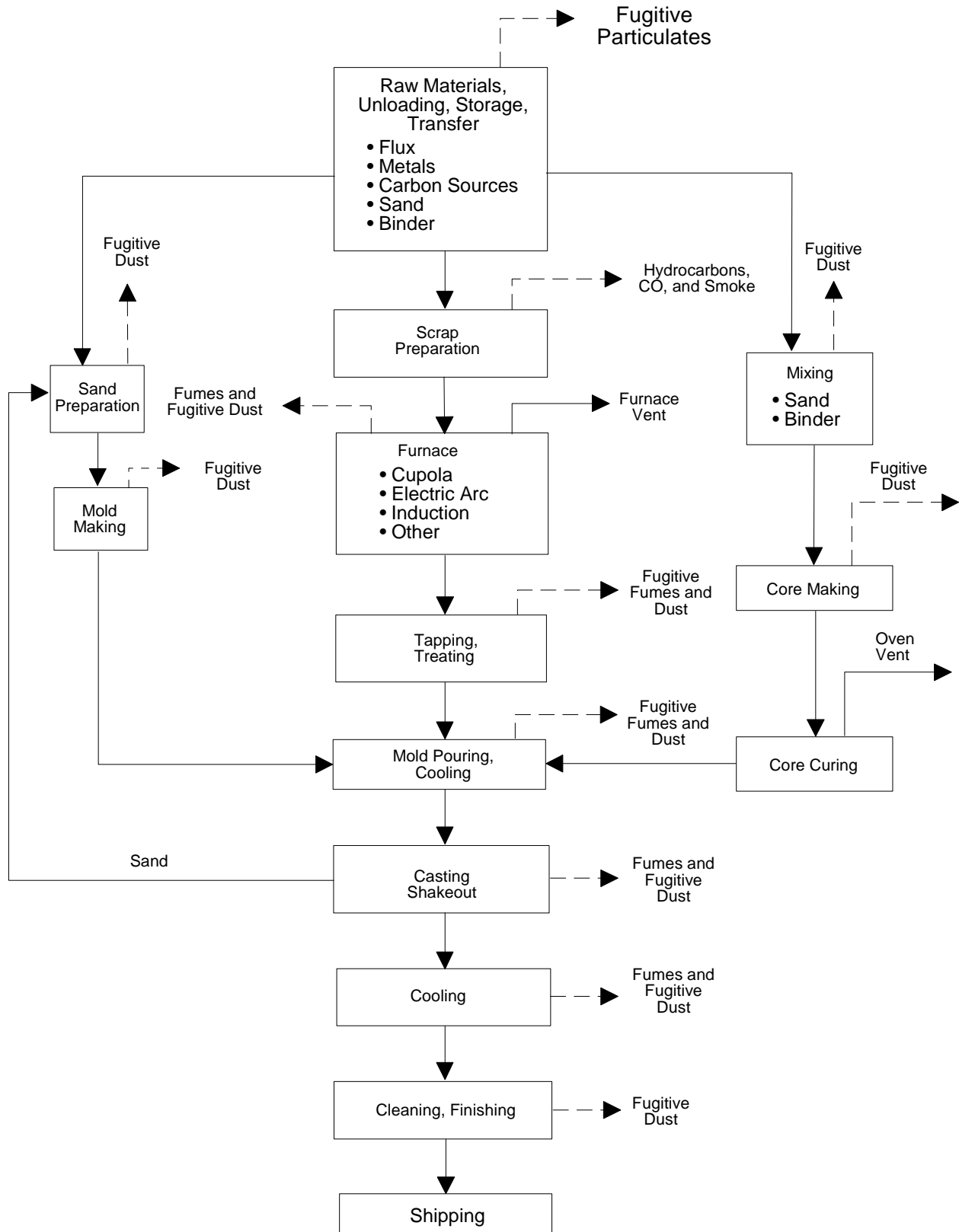


Figure 4.4.4-2. Emission Points in a Typical Iron and Steel Foundry

Source: U.S. EPA, 1995.

and transferred into the melting furnace or cupola. The charge in a furnace or cupola is heated until it reaches a certain temperature and the desired product chemistry of the melt has been attained. After the desired product is obtained, the molten metal is either poured out of the furnace into various-size teeming ladles and then into the molds or it is transferred to holding furnaces for later use.

Five foundry processes (metal melting, mold and core production, inoculation, pouring, and greensand shakeout [the removal of castings from a sand mold]) have been identified as potential sources of POM emissions. The most significant source of aromatic hydrocarbon emissions is metal melting, followed by pouring and greensand shakeout (U.S. EPA, 1990).

Metal Melting Process--The metal melting process in iron and steel foundries is accomplished primarily in cupolas, and to a lesser extent in EAFs. (See Section 4.4.3 for available emission factors for EAFs producing ferroalloys.) Cupolas are charged with alternate layers of coke, metallics, and fluxes. Combustion air is introduced into the cupola through tuyeres located at the base. The heat produced by the burning coke melts the iron, which flows down and is tapped from the bottom of the cupola. Fluxes combine with non-metallic impurities in the charge and form slag, which is removed through tap holes at the bottom of the cupola. Cupola capacities range from 1 to 30 tons (1 to 27 Mg) per hour, with a few large units capable of producing close to 100 tons (90 Mg) per hour. Larger furnaces are operated continuously, with periodic inspections and cleanings between burn cycles (U.S. EPA, 1990).

Mold and Core Production--The casting, or mold pouring and cooling operation, in iron and steel foundries has been identified as a source of POM emissions. The origin of these POM emissions is suspected to be the organic binders, including coal powder and coal tar pitch, used to form the sand molds for molten metal casting. When the hot molten metal contacts the sand mold, pyrolysis occurs and a plume of smoke is generated that contains a rich mixture of organic compounds, including POM. In addition to casting, mold preparation and casting shakeout (removal from the mold) activities have been determined to generate POM emissions. Greensand shakeout releases products of thermal decomposition of the organic chemical binders used in mold preparation.



Emission Control Techniques--POM emissions from cupolas can vary widely, depending on blast rate, blast temperature, melt rate, coke-to-melt ratio, and control technologies. Control technologies commonly used to control emissions from iron and steel foundry metal melting operations include baghouses, wet scrubbers, and afterburners. Additionally, POM emissions due to coke combustion may be reduced by substitution of gas for heat or the use of graphite as a carbon source (U.S. EPA, 1990).

Potential POM emissions from molding, casting, and shakeout appear to be a function of the type and quantity of organic binder used to produce casting molds. Emissions of POM from these foundry processes are fugitive in nature and likely exist in both particulate and gaseous forms. Fugitive emissions from such sources are generally controlled with local hooding or building ventilation systems that are ducted to a control device (predominantly baghouses) or to the atmosphere (U.S. EPA, 1990; Verma et al., 1982; Schimberg, 1980; Quilliam et al., 1985; McCalla et al., 1985).

#### Emission Factors

Data from two testing programs at a single gray iron foundry producing centrifugally cast iron pipe were averaged to develop PAH emission factors for iron foundry furnaces (EMCON, 1990; Normandeau, 1993). Emission factor data were not available for steel foundries. The emission factors for iron foundries are presented in Table 4.4.4-1. The emission source tested was a cupola, charged in a batch mode with pig iron, scrap iron, steel, coke, and limestone. Coke combined with combustion air provided the heat necessary to melt the metal, which was continuously tapped from the cupola, converted to ductile iron, and poured into steel pipe molds. Combustion gases from the cupola were vented to a gas-/oil-fired afterburner followed by a baghouse. Between the two testing programs, the facility underwent process and control device modifications to reduce emissions of toxic compounds. These modifications included an upgrade of the existing baghouse and conversion of the oil-fired afterburners to gas. The modifications resulted in a measurable reduction in PAH emissions.

TABLE 4.4.4-1. PAH EMISSION FACTORS FOR IRON FOUNDRIES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a,b</sup>	Emission Factor Rating
3-04-003-01	Cupola Furnace	Afterburner/Baghouse	Benz(a)anthracene	7.70E-06 (3.85E-06)	3.01E-06 - 1.24E-05 (1.50E-06 - 6.19E-06)	D
			Benzo(a)pyrene	3.85E-07 (1.29E-07)	1.50E-07 - 6.19E-07 (7.51E-08 - 3.10E-07)	D
			Benzo(b)fluoranthene	2.80E-06 (1.40E-06)	1.10E-06 - 4.49E-06 (5.50E-07 - 2.25E-06)	D
			Benzo(k)fluoranthene	2.37E-06 (1.18E-06)	9.42E-07 - 3.80E-06 (4.71E-07 - 1.90E-06)	D
			Chrysene	3.80E-06 (1.90E-06)	1.47E-06 - 6.12E-06 (7.36E-07 - 3.06E-06)	D
			Dibenz(a,h)anthracene	4.82E-07 (2.41E-07)	---	E
			Indeno(1,2,3-cd)pyrene	3.15E-06 (1.58E-06)	1.74E-08 - 2.12E-07 (8.68E-09 - 1.06E-07)	D
			Acenaphthene	1.15E-07 (5.73E-08)	4.91E-08 - 7.29E-08 (2.46E-08 - 3.64E-08)	D
			Acenaphthylene	6.10E-08 (3.05E-08)	1.38E-07 - 5.77E-07 (6.87E-08 - 2.88E-07)	D
			Anthracene	3.57E-07 (1.79E-07)	1.10E-06 - 5.26E-06 (5.50E-07 - 2.63E-06)	D
			Benzo(ghi)perylene	3.18E-06 (1.59E-06)	7.60E-06 - 3.17E-05 (3.80E-06 - 1.58E-05)	D
			Fluorene	7.93E-08 (3.96E-08)	---	E

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(continued)

TABLE 4.4.4-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a,b</sup>	Emission Factor Rating
3-04-003-01	Cupola Furnace	Afterburner/Baghouse	Fluoranthene	1.96E-05 (9.82E-06)	1.36E-06 - 5.62E-06 (6.79E-07 - 2.81E-06)	D
			Naphthalene	1.68E-07 (8.42E-08)	5.56E-06 - 2.32E-05 (2.78E-06 - 1.16E-05)	D
			Phenanthrene	3.49E-06 (1.74E-06)	0.00E+00 - 0.00E+00 (0.00E+00 - 0.00E+00)	D
			Pyrene	1.44E-05 (7.18E-06)	4.82E-07 - 0.00E+00 (2.41E-07 - 0.00E+00)	D

<sup>a</sup>Emission factors are in lb (Kg) of pollutant emitted per ton (Mg) of cast pipe produced.

<sup>b</sup>Ranges represent averaged data from two test reports (single facility).

Source: EMCON, 1990; Normandeau, 1993.

## Source Locations

Based on a survey conducted by the EPA in support of the iron and steel foundry Maximum Achievable Control Technology (MACT) standard development, there were 755 iron and steel foundries in the United States in 1992 (Maysilles, 1993). Foundry locations can be correlated with areas of heavy industry and manufacturing and, in general, with the iron and steel production industry (Ohio, Pennsylvania, and Indiana).

Additional information on iron and steel foundries and their locations may be obtained from the following trade associations:

- American Foundrymen's Society, Des Plaines, Illinois;
- National Foundry Association, Des Plaines, Illinois;
- Ductile Iron Society, Mountainside, New Jersey;
- Iron Casting Society, Warrendale, Pennsylvania; and
- Steel Founders' Society of America, Des Plaines, Illinois.

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#### 4.4.5 Secondary Lead Smelting

##### Process Description

The secondary lead smelting industry produces elemental lead and lead alloys by reclaiming lead, mainly from scrap automobile batteries. Blast, reverberatory, rotary, and electric furnaces are used for smelting scrap lead and producing secondary lead. Smelting is the reduction of lead compounds to elemental lead in a high-temperature furnace, which requires higher temperatures (2,200 to 2,300°F [1,200 to 1,260°C]) than those required for melting elemental lead (621°F [327°C]). Secondary lead may be refined to produce soft lead (which is nearly pure lead) or alloyed to produce hard lead. Most of the lead produced by secondary lead smelters is hard lead that is used in the production of lead-acid batteries (U.S. EPA, 1994a).

Lead-acid batteries represent about 90 percent of the raw materials at a typical secondary lead smelter, although this percentage may vary from one plant to the next. These batteries contain approximately 18 lb (8.2 kg) of lead per battery consisting of 40 percent lead alloys and 60 percent lead oxide. Other types of lead-bearing raw materials recycled by secondary lead smelters include drosses (lead-containing byproducts of lead refining), which may be purchased from companies that perform lead alloying or refining but not smelting; battery plant scrap, such as defective grids or paste; and scrap lead, such as old pipes or roof flashing. Other scrap lead sources include cable sheathing, solder, and babbitt-metal (U.S. EPA, 1994a).

POM emissions from secondary lead smelters are expected to occur from the combustion of the polymeric organic casings (plastic and rubber) on batteries (Bennet et al., 1979, National Research Council, 1983).

As illustrated in Figure 4.4.5-1, the normal sequence of operations in a secondary lead smelter is scrap receiving, charge preparation, furnace smelting, and lead refining and alloying. In the majority of plants, scrap batteries are first sawed or broken open to remove the lead alloy plates and lead oxide paste material. The removal of battery covers is typically accomplished using an automatic battery feed conveyor system and a slow-speed saw. Hammer

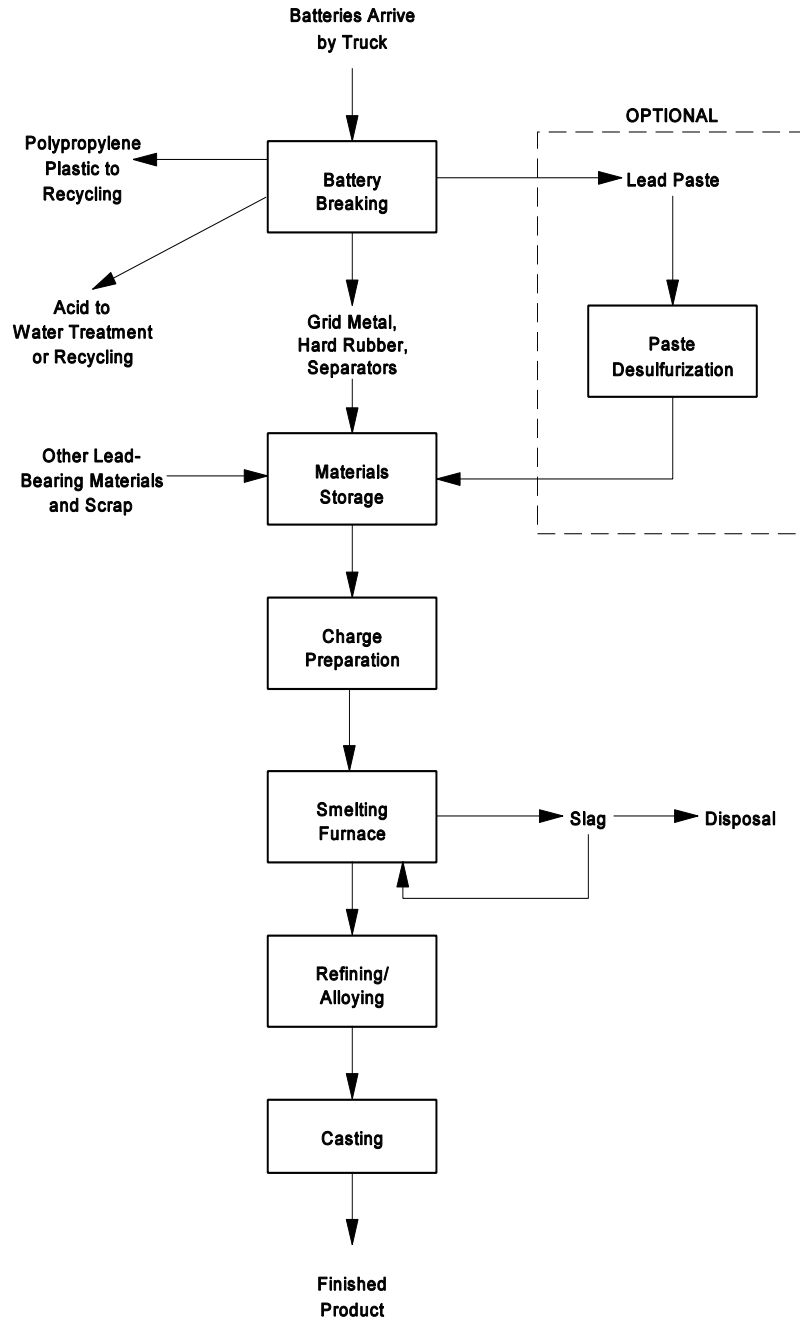


Figure 4.4.5-1. Simplified Process Flow Diagram for Secondary Lead Smelting

Source: U.S. EPA, 1994a.

mills or other crushing/shredding devices are then used to break open the battery cases. Float/sink separation systems are typically used to separate plastic battery parts, lead terminals, lead oxide paste, and rubber parts. The majority of lead smelters recover the crushed plastic materials for recycling. Rubber casings are usually landfilled.

Paste desulfurization, an optional lead recovery step used by secondary lead smelters, requires the separation of lead sulfate and lead oxide paste from the lead grid metal, polypropylene plastic cases, separators, and hard rubber battery cases. Paste desulfurization involves the chemical removal of sulfur from the lead battery paste. The process improves furnace efficiency by reducing the need for fluxing agents to reduce lead-sulfur compounds to lead metal. The process also reduces sulfur dioxide (SO<sub>2</sub>) furnace emissions. However, SO<sub>2</sub> emissions reduction is usually a less important consideration because many plants that perform paste desulfurization are also equipped with SO<sub>2</sub> scrubbers. About one-half of smelters perform paste desulfurization (U.S. EPA, 1994a).

After removing the lead components from the charge batteries, the lead scrap is combined with other charge materials such as refining drosses, flue dust, furnace slag, coke, limestone, sand, and scrap iron and fed to either a reverberatory, blast, rotary or electric smelting furnace. Smelting furnaces are used to produce crude lead bullion, which is refined and/or alloyed into final lead products. There are currently about 15 reverberatory furnaces, 24 blast furnaces, 5 rotary furnaces, and 1 electric furnace operating in the secondary lead industry in the United States (U.S. EPA, 1994a). Blast and reverberatory furnaces are currently the most common types of smelting furnaces used in the industry, although some new plants are using rotary furnaces.

Reverberatory Furnaces--A reverberatory furnace (Figure 4.4.5-2) is a rectangular refractory-lined furnace. Reverberatory furnaces are operated on a continuous basis. Natural gas- or fuel oil-fired jets located at one end, or at the sides, of the furnace are used to heat the furnace and charge material to an operating temperature of about 2,000°F (1,100°C). Oxygen enrichment may be used to decrease the combustion air requirements. Reverberatory furnaces are maintained at negative pressure by an induced draft fan.



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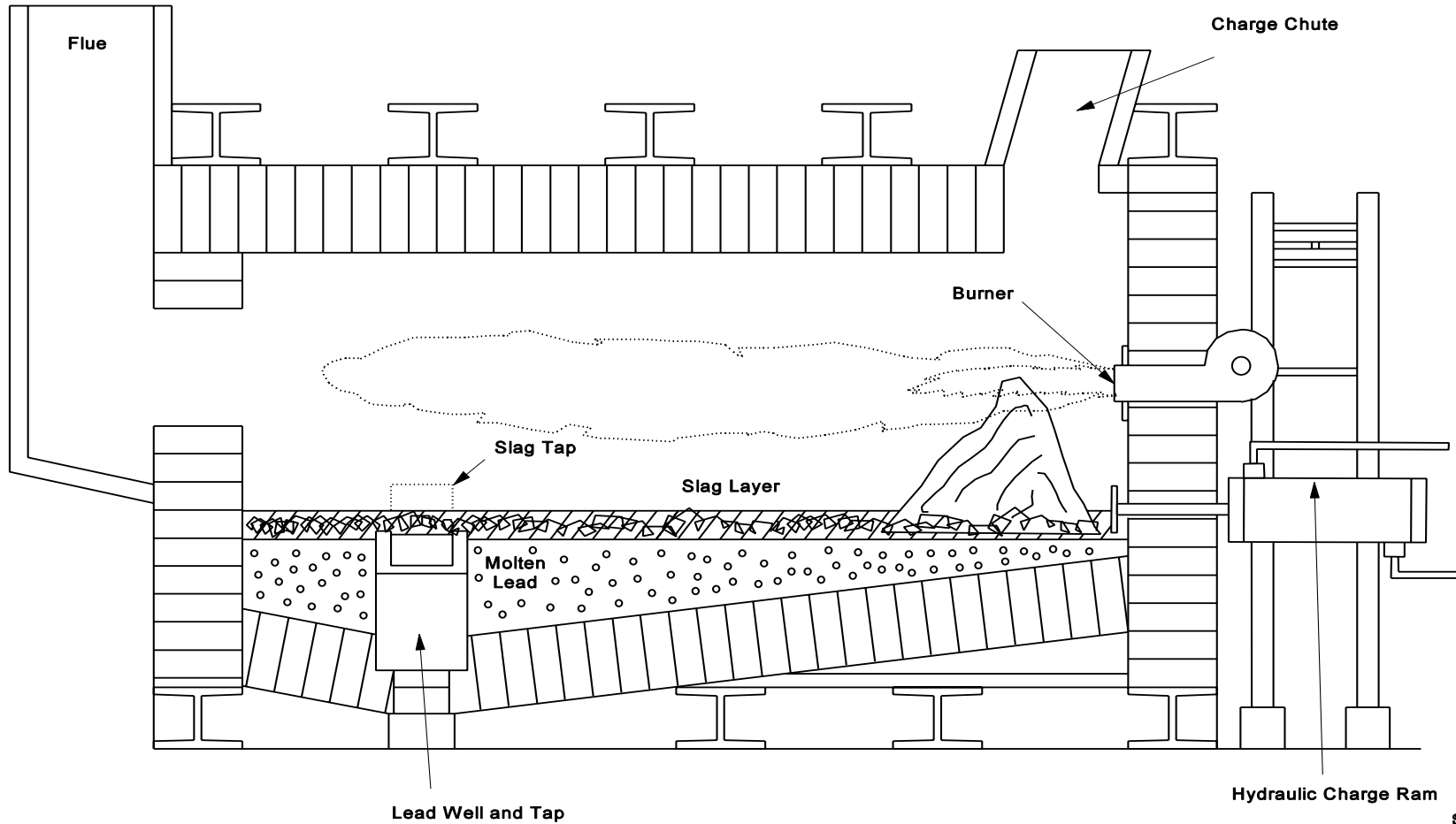
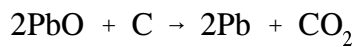
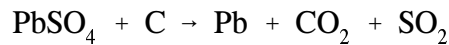


Figure 4.4.5-2. Cross-Sectional View of a Typical Stationary Reverberatory Furnace

Source: U.S. EPA, 1994a.

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Reverberatory furnaces are used to produce a soft (nearly pure) lead product and a lead-bearing slag. This is done by controlling the reducing conditions in the furnace so that lead components are reduced to metallic lead bullion while the alloying elements (antimony, tin, arsenic) in the battery grids, posts, straps, and connectors are oxidized and removed in the slag. The reduction of  $\text{PbSO}_4$  and  $\text{PbO}$  is promoted by the carbon-containing coke added to the charge material:



The  $\text{PbSO}_4$  and  $\text{PbO}$  also react with the alloying elements to form lead bullion and oxides of the alloying elements, which are removed in the slag.

The molten lead collects in a pool at the lowest part of the hearth. Slag collects in a layer on top of this pool and retards further oxidation of the lead. The slag is made up of molten fluxing agents such as iron, silica, and lime, and typically has significant quantities of lead. Slag is usually tapped continuously and lead is tapped intermittently. The slag is tapped into a crucible. The slag tap and crucible are hooded and vented to a control device. Reverberatory furnace slag usually has a high lead content (as much as 70 percent by weight) and is used as feed material in a blast or electric furnace to recover the lead content. Reverberatory furnace slag may also be rerun through the reverberatory furnace during special slag campaigns before being sent to a blast or electric furnace. Lead may be tapped into a crucible or directly into a holding kettle. The lead tap is usually hooded and vented to a control device (U.S. EPA, 1994a).

Blast Furnaces--A blast furnace (Figure 4.4.5-3) is a vertical furnace that consists of a crucible with a vertical cylinder affixed to the top. The crucible is refractory-lined and the vertical cylinder consists of a steel water-jacket. Oxygen-enriched combustion air is introduced into the furnace through tuyeres located around the base of the cylinder.

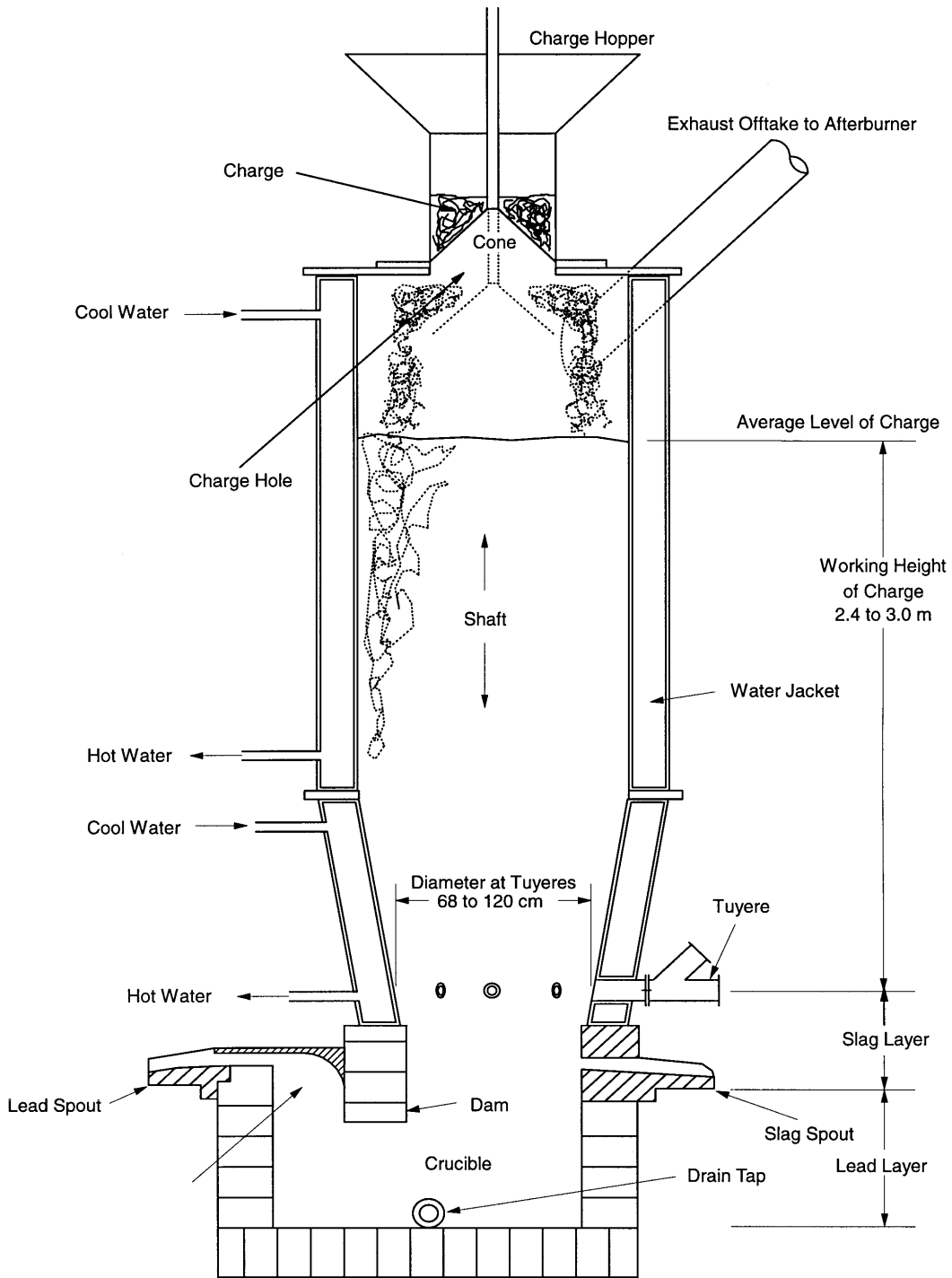


Figure 4.4.5-3. Cross-section of Typical Blast Furnace

Source: U.S. EPA, 1994a.

Charge materials are pre-weighed to ensure the proper mixture and then introduced into the top of the cylinder using a skip hoist, a conveyor, or a front-end loader. The charge fills nearly the entire cylinder. Charge material is added periodically to keep the level of the charge at a consistent working height while lead and slag are tapped from the crucible. Coke is added to the charge as the primary fuel, although natural gas jets may be used to start the combustion process. Combustion is self-sustaining as long as there is sufficient coke in the charge material. Combustion occurs in the layer of the charge nearest the tuyeres.

At plants that operate only blast furnaces, the lead-bearing charge materials may include broken battery components, drosses from the refining kettles, agglomerated flue dust, and lead-bearing slag. A typical charge over one hour may include 4.8 tons (4.4 Mg) of grids and paste, 0.3 tons (0.3 Mg) of coke, 0.1 tons (0.1 Mg) of calcium carbonate, 0.07 tons (0.06 Mg) of silica, 0.5 tons (0.4 Mg) of cast iron, and 0.2 tons (0.2 Mg) of rerun blast furnace slag, to produce 3.7 tons (3.4 Mg) of lead. At plants that also have a reverberatory furnace, the charge materials will also include lead-bearing reverberatory furnace slag (U.S. EPA, 1994a).

Blast furnaces are designed and operated to produce a hard (high alloy content) lead product by achieving more reducing furnace conditions than those typically found in a reverberatory furnace. Fluxing agents include iron, soda ash, limestone, and silica (sand). The oxidation of the iron, limestone, and silica promotes the reduction of lead compounds and prevents oxidation of the lead and other metals. The soda ash enhances the reaction of  $\text{PbSO}_4$  and  $\text{PbO}$  with carbon from the coke to reduce these compounds to lead metal.

Lead tapped from a blast furnace has a higher content of alloying metals (up to 25 percent) than lead produced by a reverberatory furnace. In addition, much less of the lead and alloying metals are oxidized and removed in the slag, so the slag has a low metal content (e.g., 1 to 3 percent) and frequently qualifies as a nonhazardous solid waste.

Because air is introduced into the blast furnace at the tuyeres, blast furnaces are operated at positive pressure. The operating temperature at the combustion layer of the charge is

between 2,200 and 2,600°F (1,200 and 1,400°C), but the temperature of the gases exiting the top of the charge material is between 750 and 950°F (400 and 500°C).

Molten lead collects in the crucible beneath a layer of molten slag. As in a reverberatory furnace, the slag inhibits the further oxidation of the molten metal. Lead is tapped continuously and slag is tapped intermittently, slightly before it reaches the level of the tuyeres. If the tuyeres become blocked with slag, they are manually or automatically “punched” to clear the slag. A sight glass on the tuyeres allows the furnace operator to monitor the slag level and ensure that the tuyeres are clear of slag. At most facilities, the slag tap is temporarily sealed with a clay plug, which is driven out to begin the flow of slag from the tap into a crucible. The slag tap and crucible are enclosed in a hood, which is vented to a control device.

A weir dam and siphon in the furnace are used to remove the lead from beneath the slag layer. Lead is tapped from a blast furnace into either a crucible or directly to a refining kettle designated as a holding kettle. The lead in the holding kettle is kept molten before being pumped to a refining kettle for refining and alloying. The lead tap on a blast furnace is hooded and vented to a control device.

Rotary Furnaces--As noted above, rotary furnaces (sometimes referred to as rotary reverberatory furnaces) (Figure 4.4.5-4) are used at only a few recently constructed secondary lead smelters in the United States (U.S. EPA, 1994a). Rotary furnaces have two advantages over other furnace types: the ease of adjusting the relative amount of fluxing agents (because the furnaces are operated on a batch rather than a continuous basis), and a better mix of the charge materials.

A rotary furnace consists of a refractory-lined steel drum mounted on rollers with a variable-speed motor to rotate the drum. An oxygen-enriched natural gas or fuel oil jet at one end of the furnace heats the charge material and the refractory lining of the drum. The connection to the flue is located at the same end as the jet. A sliding door at the end of the furnace opposite the jet allows charging of material to the furnace. Charge materials are typically placed in the furnace using a retractable conveyor or charge bucket, although other methods are possible.

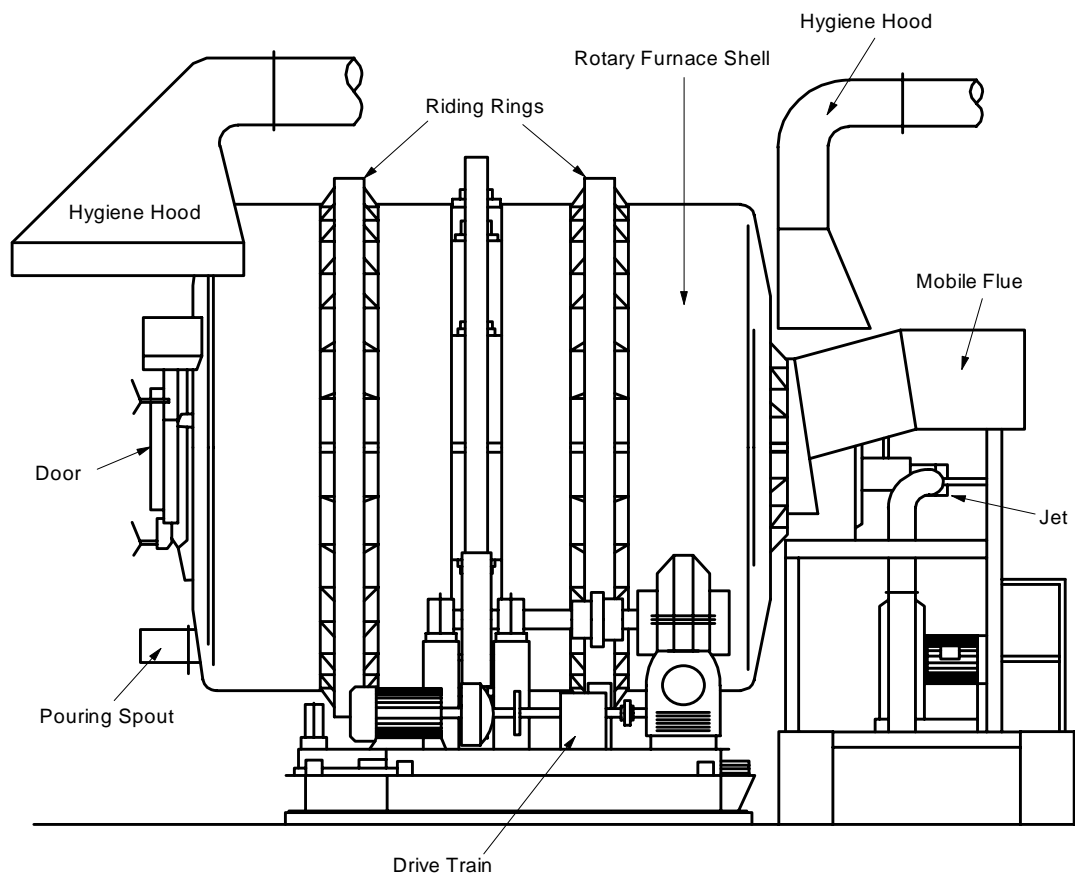


Figure 4.4.5-4. Side View of a Typical Rotary Reverberatory Furnace

Source: U.S. EPA, 1994a.

Lead-bearing raw materials charged to rotary furnaces include broken battery components, flue dust, and drosses. Rotary furnaces can use the same lead-bearing raw materials as reverberatory furnaces, but they produce slag that is relatively free of lead, less than 2 percent. As a result, a blast furnace is not needed for recovering lead from the slag, which can be disposed of as a nonhazardous waste.

Fluxing agents for rotary furnaces may include iron, silica, soda ash, limestone, and coke. The fluxing agents are added to promote the conversion of lead compounds to lead metal. Coke is used as a reducing agent rather than as a primary fuel. A typical charge may consist of 12 tons (11 Mg) of wet battery scrap, 0.8 tons (0.7 Mg) of soda ash, 0.6 tons (0.5 Mg) of coke, and 0.6 tons (0.5 Mg) of iron, and will yield approximately 9 tons (8 Mg) of lead product (U.S. EPA, 1994a).

The lead produced by rotary furnaces is a semi-soft lead with an antimony content somewhere between that of lead from reverberatory and blast furnaces. Lead and slag are tapped from the furnace at the conclusion of the smelting cycle. Each batch takes 5 to 12 hours to process, depending on the size of the furnace. Like reverberatory furnaces, rotary furnaces are operated at a slight negative pressure.

Electric Furnaces--An electric furnace consists of a large, steel, kettle-shaped container that is refractory-lined (Figure 4.4.5-5). A cathode extends downward into the container and an anode is located in the bottom of the container. Second-run reverberatory furnace slag is charged into the top of the furnace. Lead and slag are tapped from the bottom and side of the furnace, respectively. A fume hood covering the top of the furnace is vented to a control device.

In an electric furnace, electric current flows from the cathode to the anode through the scrap charge. The electrical resistance of the charge causes the charge to heat up and become molten. There is no combustion process involved in an electric furnace.

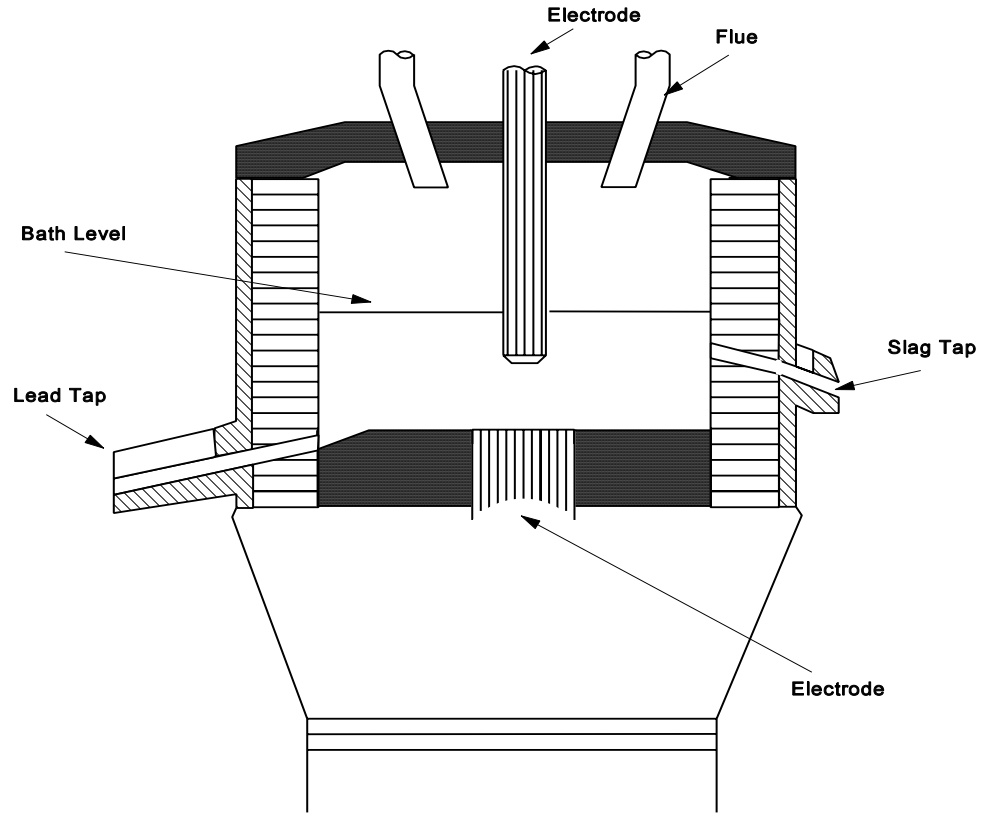


Figure 4.4.5-5. Cross-Sectional View of an Electric Furnace for Processing Slag.

Source: U.S. EPA, 1994a.



There is only one known electric furnace in operation in the U.S. for the secondary lead industry. It is used to process second-run reverberatory furnace slag, and it fulfills the same role as a blast furnace used in conjunction with a reverberatory furnace. However, the electric furnace has two advantages over a blast furnace. First, because there are no combustion gases, ventilation requirements are much lower than for blast or reverberatory furnaces, and the potential for POM formation and emissions is greatly reduced. Second, the electric furnace is extremely reducing, and produces a glass-like, nearly lead-free slag that is nonhazardous (U.S. EPA, 1994a).

Refining, the final step in secondary lead production, consists of removing impurities and adding alloying metals to the molten lead obtained from the smelting furnaces to meet a customer's specifications. Refining kettles are used for the purifying and alloying of molten lead.

Emission Control Techniques--Controls used to reduce organic emissions from smelting furnaces in the secondary lead smelting industry include afterburners on blast furnaces and combined blast and reverberatory exhausts. Reverberatory and rotary furnaces have minimal POM emissions because of high exhaust temperatures and turbulence, which promote complete combustion of organics. No controls for total hydrocarbons (THC) are necessary for these process configurations (U.S. EPA, 1994b).

POM emissions from blast furnaces are dependent on the type of add-on control used. An afterburner operated at 1,300°F (700°C) achieves about 90 percent destruction efficiency of THC, including POM. Facilities with blast and reverberatory furnaces usually combine the exhaust streams and vent the combined stream to an afterburner. The higher operating temperature of the reverberatory furnace reduces the fuel needs of the afterburner so that the afterburner is essentially "idling." Any temperature increase measured across the afterburner is due to the heating value of organic compounds in the blast furnace exhaust. A combined reverberatory and blast furnace exhaust stream ducted to an afterburner with an exit temperature of 1,700°F (930°C) can achieve 98 percent destruction efficiency for THC (U.S. EPA, 1994b).

Additional controls used by secondary lead smelters include baghouses for particulate and metals control, hooding and ventilation to a baghouse for process fugitives, and scrubbers for hydrochloric acid (HCl) and SO<sub>2</sub> control.

#### Emission Factors

Process emissions (i.e., those emitted from the smelting furnace's main exhaust) contain metals, organics (including POM), HCl, and chlorine (Cl<sub>2</sub>). Process emissions also contain criteria pollutants, including particulate matter (PM), volatile organic compounds (VOC), carbon monoxide (CO), and SO<sub>2</sub>.

Blast furnaces are substantially greater sources of POM emissions than are reverberatory or rotary furnaces. Low exhaust temperatures from the charge column (about 800°F [430°C]) result in the formation of products of incomplete combustion from the organic material in the feed material. Uncontrolled THC emissions from a typical 50,000 Mg/yr blast furnace are about 310 tpy (280 Mg/yr) (U.S. EPA, 1994a).

Controlled blast furnace POM emissions are dependent on the add-on controls that are used, which may be from 80 to 99 percent effective at reducing THC emissions. Rotary and reverberatory furnaces have much higher exhaust temperatures than blast furnaces, about 1,800 to 2,200°F (980 to 1,200°C), and have much lower THC emissions because of more complete combustion. THC emissions from a typical rotary furnace (15,000 Mg/yr capacity) are about 38 tpy (34 Mg/yr). The majority of these emissions occur during furnace charging, when the burner is cut back and the temperature is reduced. Emissions drop off sharply when charging is completed and the is brought to normal operating temperature (U.S. EPA, 1994a).

POM emissions from reverberatory furnaces are even lower than those from rotary furnaces because reverberatory furnaces are operated continuously rather than on a batch basis.

Test reports from three separate secondary lead smelters were used to develop POM emission factors (Roy F. Weston, Inc, 1993a,b,c). All testing was conducted in support of

the U.S. EPA Secondary Lead National Emission Standards for Hazardous Air Pollutants (NESHAP) program. The three facilities tested represent the following process configurations: a rotary smelting furnace equipped with a baghouse and SO<sub>2</sub> scrubber; a blast furnace equipped with an afterburner, baghouse, and SO<sub>2</sub> scrubber; and a reverberatory and blast furnace with exhaust from each furnace combined prior to a single afterburner, baghouse and SO<sub>2</sub> scrubber.

Uncontrolled semi-volatile organic compound emissions were measured at all three facilities using a semi-volatile organic sampling train (EPA Reference Method SW846-0010). The semi-VOST sampling train captures both particulate and vaporous POM compounds. PAHs were measured at the blast furnace outlet (before the afterburner) at two facilities, and at the rotary furnace outlet at one facility. THC emissions were measured at both the blast furnace and rotary furnace outlets and at the afterburner outlets following the blast furnaces. Three PAH compounds were analyzed at the tested facilities: naphthalene, chrysene, and pyrene. Emission factors for these PAHs are shown in Table 4.4.5-1. Although PAH emissions were not measured after the control device (afterburner or combined reverberatory and blast furnace exhaust), controlled emission factors were estimated using the THC control efficiency for the given process configuration. These estimates assume that the control efficiency for the PAH species detected was equal to the control efficiency for THC.

One additional set of data has been identified that quantifies POM emissions from a secondary lead smelter processing batteries (Bennet, 1979). In this study, four emission samples were obtained from one facility. The data measured were PAH concentrations in the stack gases following the final control device. The type of control device used was not specified. The predominant PAHs measured were anthracene/phenanthrene and fluoranthene. Benzo(a)pyrene was measured, but at levels only 0.1 percent of the anthracene/phenanthrene levels.

TABLE 4.4.5-1. PAH EMISSION FACTORS FOR SECONDARY LEAD SMELTING

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg)	Emission Factor Rating	Reference
3-04-004-03	Blast Furnace	None	Naphthalene	0.182 (0.0911) <sup>b</sup>	0.0602 - 0.304 (0.0301 - 0.152)	D	Weston, 1993a,b; U.S. EPA, 1994c
3-04-004-03	Blast Furnace	Afterburner	Naphthalene	0.0125 (6.26E-03) <sup>b</sup>	4.33E-4 - 0.0246 (2.16E-4 - 0.0123)	D	Weston, 1993a,b; U.S. EPA, 1994c
3-04-004-04	Rotary Furnace	None	Chrysene	1.83E-03 (9.17E-04)	---	D	Weston, 1993c
			Pyrene	7.22E-04 (3.61E-04)	---	D	Weston, 1993c

<sup>a</sup>Emission factors in lb/ton (kg/Mg) of lead smelted.

<sup>b</sup>Average emission factor from two facility test reports.

The sampling and analytical procedures used during the tests were capable of capturing and measuring both particulate and vapor phase POM. The majority of the POM measured was caught in the water impingers. The average stack gas concentrations (ng/Nm<sup>3</sup>) of four samples taken on two site visits to the same smelter were anthracene/phenanthrene 762.5; methyl anthracenes 33.25; fluoranthene 970; pyrene 27.75; methyl pyrenes/fluoranthenes 2.25; benzo(c)phenanthrene 12.75; chrysene/benz(a)anthracene 25.25; and benzo(a)pyrene 1 (Bennet et al., 1979).

#### Source Locations

In 1990, primary and secondary smelters in the United States produced 1,380,000 tons (1,255,000 Mg) of lead. Secondary lead smelters produced 946,000 tons (860,000 Mg) or about 69 percent of the total refined lead produced in 1990, and primary smelters produced 434,000 tons (395,000 Mg) (U.S. EPA, 1994a). Table 4.4.5-2 lists U.S. secondary lead smelters according to their annual lead production capacity.

TABLE 4.4.5-2. U.S. SECONDARY LEAD SMELTERS GROUPED  
ACCORDING TO ANNUAL LEAD PRODUCTION CAPACITY

Smelter	Location
<u>Small-Capacity Group:</u> <sup>a</sup>	
Delatte Metals	Ponchatoula, LA
General Smelting and Refining Company	College Grove, TN
Master Metals, Inc.	Cleveland, OH
Metals Control of Kansas	Hillsboro, KS
Metals Control of Oklahoma	Muskogee, OK
<u>Medium-Capacity Group:</u> <sup>b</sup>	
Doe Run Company	Boss, MO
East Penn Manufacturing Company	Lyon Station, PA
Exide Corporation	Muncie, IN
Exide Corporation	Reading, PA
GNB, Inc.	Columbus, GA
GNB, Inc.	Frisco, TX
Gulf Coast Recycling, Inc.	Tampa, FL
Refined Metals Corporation	Beech Grove, IN
Refined Metals Corporation	Memphis, TN
RSR Corporation	City of Industry, CA
RSR Corporation	Middletown, NY
Schuylkill Metals Corporation	Forest City, MO
Tejas Resources, Inc.	Terrell, TX
<u>Large-Capacity Group:</u> <sup>c</sup>	
Gopher Smelting and Refining, Inc.	Eagan, MN
GNB, Inc.	Vernon, CA
RSR Corporation	Indianapolis, IN
Sanders Lead Company	Troy, AL
Schuylkill Metals Corporation	Baton Rouge, LA

<sup>a</sup>Less than 22,000 tons (20,000 Mg).

<sup>b</sup>22,000 to 82,000 tons (20,000 to 75,000 Mg).

<sup>c</sup>Greater than 82,000 tons (75,000 Mg).

Source: U.S. EPA, 1994a.

#### SECTION 4.4.5 REFERENCES

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## 4.5 PETROLEUM REFINING

Crude oil contains small amounts of naturally occurring aromatics, including some POM, that may be emitted from some processes and operations at petroleum refineries. Other processes may form POM, which may be emitted at the point of generation or downstream in another operation. A flow diagram of processes likely to be found at a model refinery is shown in Figure 4.5-1. The arrangement of these processes varies among refineries, and few, if any, employ all of these processes.

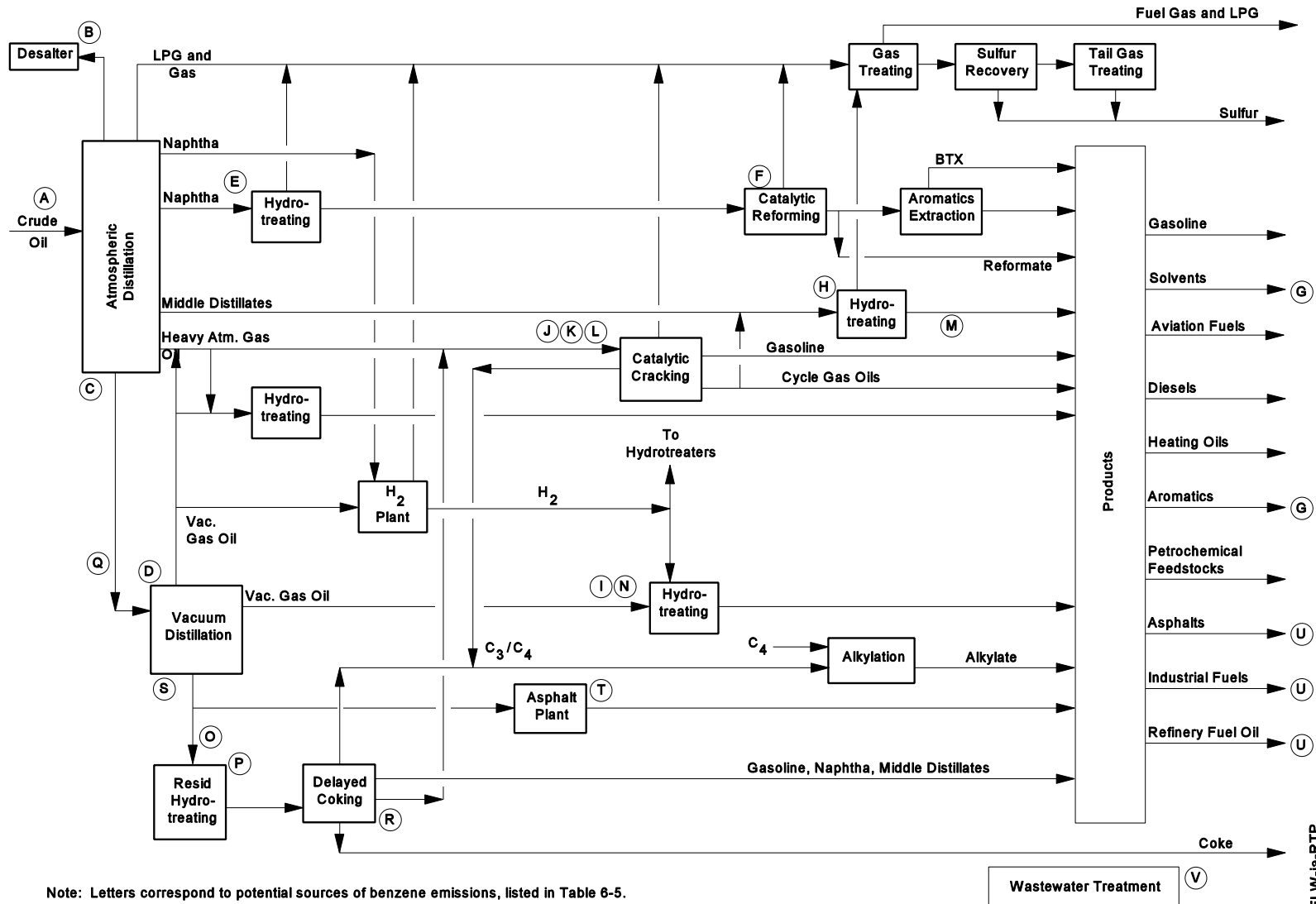
Processes at petroleum refineries can be grouped into five types: (1) separation processes, (2) conversion processes, (3) treating processes, (4) auxiliary processes and operation, and (5) feedstock/product storage and handling. These operations are discussed briefly below.

The first phase in petroleum refining operations is the separation of crude oil into its major constituents using four separation processes: (1) desalting, (2) atmospheric distillation, (3) vacuum distillation, and (4) light ends recovery.

To meet the demands for high-octane gasoline, jet fuel, and diesel fuel, components such as residual oils, fuel oils, and light ends are converted to gasolines and other light fractions using one or more of the following conversion processes: (1) catalytic cracking (fluidized-bed and moving-bed), (2) thermal processes (coking, and visbreaking), (3) alkylation, (4) polymerization, (5) isomerization, and (6) reforming.

Petroleum treating processes stabilize and upgrade petroleum products by separating them from less desirable products. Among the treating processes are (1) hydrotreating, (2) chemical sweetening, (3) de-asphalting, and (4) asphalt blowing.





Note: Letters correspond to potential sources of benzene emissions, listed in Table 6-5.

Figure 4.5-1. Process Flow Diagram for a Model Petroleum Refinery

Auxiliary processes and operations include process heaters and stationary compressor engines (emissions from which are discussed in other sections of this document), sulfur recovery units, blowdown systems, flares, cooling towers, and wastewater treatment facilities.

Finally, all refineries have a feedstock/product storage area (commonly called a “tank farm”) with storage tanks whose capacities range from less than 1,000 barrels to more than 500,000 barrels. Feedstock/product handling operations (transfer operations) consist of the loading and unloading of transport vehicles (including trucks, rail cars, and marine vessels). Emissions that are associated with these operations are discussed in Section 4.12.8 as part of gasoline distribution and marketing.

Emissions of HAPs from the different processes in petroleum refineries have been investigated recently in support of Federal NESHAP development; a MACT standard for the petroleum refinery source category was promulgated in 1995. The investigations did not focus on POM because of their relative insignificance compared to lighter aromatics. However, some indications of total POM quantities emitted from various processes did surface, and emissions of one PAH, naphthalene, were detected from some processes, which were not reported previously.

In general, the largest sources of POM emissions from petroleum refinery processes are process heaters and catalytic cracking units. Process heater emissions are discussed in Section 4.1.2 of this document; emissions from FCC units are discussed next. Other sources of POM emissions, primarily naphthalene, include process vents on the sulfur recovery, thermal coking, and blowdown systems, and from wastewater. Because the data for emissions from these sources are limited and the emissions are relatively minor, the sources are not described in detail; rather, emissions and controls are summarized in Section 4.5.2.

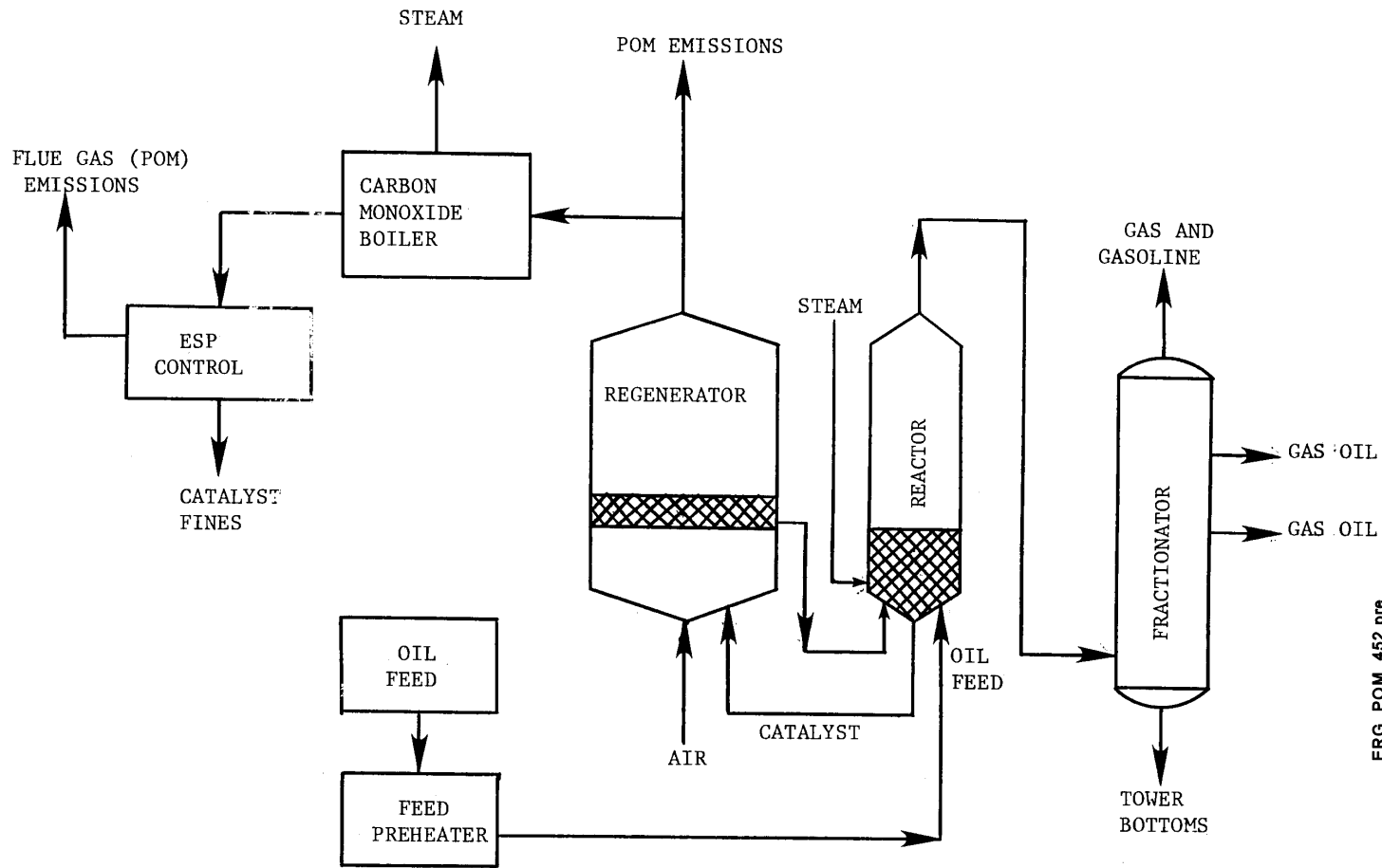
#### 4.5.1 Catalytic Cracking Units

##### Process Description

Catalytic cracking processes are the means by which the production of gasoline can be substantially increased from a given amount of crude oil. Heavier feedstocks such as atmospheric or vacuum gas oils are cracked in fluidized or moving-bed units to produce slurry oil, light cycle oil, cracked gasoline, light gases, and coke (Radian, 1980). The cracking takes place in the presence of a catalyst, which can become deactivated through the continual deposition of coke (i.e., carbon) on active sites. To combat catalyst degradation, catalysts are regenerated by combusting the coke deposits on the catalyst. This combustion of coke during catalyst regeneration has been found to form POM emissions (Hangebrauck et al., 1967).

Two types of catalytic crackers are used in the petroleum industry: fluidized-bed and moving-bed designs. There are two types of moving-bed designs: Thermoform<sup>®</sup> catalytic cracking (TCC) units and Houdrifiow<sup>®</sup> catalytic cracking (HCC) units. Fluidized-bed catalytic crackers (FCC) greatly dominate over the moving-bed type, constituting well over 90 percent of total cracking feed capacity. The industry has been generally phasing out the use of moving-bed units since 1980 in favor of the more efficient FCC units (Radian, 1980).

A process flow diagram of a typical FCC unit is shown in Figure 4.5-2 (Radian, 1980). In the FCC process, hot regenerated catalyst, mixed with hydrocarbon feed, is transported into the cracking reactor. The reactor, which is maintained at about 900°F (480°C) and 15 psig, contains a bed of powdered silica-alumina type catalyst which is kept in a fluidized state by the flow of vaporized feed material and steam (Radian, 1980; Hangebrauck et al., 1967). Cracking of the feed, which occurs in the riser leading to the reactor and in the fluidized bed, causes a deposit of coke to form on the catalyst particles. A continuous stream of spent catalyst is withdrawn from the reactor and steam-stripped to remove hydrocarbons. The catalyst particles are then pneumatically conveyed to a catalyst regeneration unit. Hydrocarbon vapors from the cracking process are fractionated in a distillation column to produce light hydrocarbons, cracked gasoline, and fuel oil (Radian, 1980).



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Figure 4.5-2. Diagram of a Fluid-Bed Catalytic Cracking Process

Source: Radian, 1980.

In the catalyst regeneration unit, coke deposits are burned off at temperatures nearly 1,000°F (540°C) and pressures ranging from 2 to 20 psig (Hangebrauck, 1967). This coke combustion process is the source of POM emissions in the regeneration portion of FCC units (Radian, 1980; Hangebrauck, 1967). The regenerated catalyst is continuously returned to the cracking reactor. Heat added to the catalyst during regeneration (coke combustion) furnishes much of the required heat for the cracking reaction (Radian, 1980). Uncontrolled regenerator flue gases contain a high amount of CO along with other unburned hydrocarbons (potentially including POM compounds). These flue gases can be vented directly to the atmosphere or to a CO waste heat boiler (Radian, 1980; Hangebrauck et al., 1967).

Moving-bed cracking units are similar to FCC units but use beaded or pelleted catalysts (Radian, 1980; Hangebrauck et al., 1967). In both TCC and HCC units, the cracking process is initiated by having regenerated catalyst and vaporized hydrocarbon feed enter the top of the cracking reactor chamber and travel co-currently downward through the vessel. As the cracking process proceeds, synthetic crude product is withdrawn and sent to the synthetic crude distillation tower for processing into light fuels, heavy fuels, catalytic gasoline, and wet gas (Radian, 1980). At the base of the reactor, the catalyst is purged with steam to remove hydrocarbons and is then gravity fed into the catalyst regeneration chamber.

In the regeneration chamber, combustion air is added at a controlled rate to burn off catalyst coke deposits. As in FCC units, burning coke produces POM emissions that are released in TCC and HCC catalyst regenerator flue gases. Regenerated catalyst is collected at the bottom of the chamber and is conveyed by airlift to a surge hopper above the cracking reactor where it can be gravity-fed back into the cracking process (Radian, 1980).

Flue gases from TCC and HCC units are either vented directly to the atmosphere or to a CO waste heat boiler. Waste heat boilers that are fired with an auxiliary fuel or contain a catalyst are reported to have been 99 percent efficient in reducing PAH emissions from a regeneration unit (Radian, 1980). In several installations, particulate matter emissions from the waste heat boiler are controlled by an ESP (Radian, 1980). Catalytic cracking units constructed after June 1973 are subject to a new source performance standard that limits CO and particulate

matter emissions to such a level that a waste heat boiler and ESP are generally required for compliance (Radian, 1980). Cyclones and scrubbers have also been used for added control.

Some TCC units have also been equipped in some installations with direct-fired afterburners called plume burners. The plume burner is a secondary stage of combustion built into the catalyst regeneration chambers. This type of burner successfully increases the clarity of plumes from regeneration flue gases; however, compared to a CO waste heat boiler, the plume burner is ineffective at reducing POM emissions (Hangebrauck, 1967).

Another way to reduce POM emissions from the catalyst regenerators is to achieve a more complete combustion of CO to CO<sub>2</sub>. Processes such as the Universal Oil Products (UOP) hot regeneration and Amoco Ultracat<sup>®</sup> have been developed to aid in the achievement of lower overall POM emissions. The relatively higher temperatures for catalyst regeneration used in the UOP process serves to improve coke combustion efficiency and thus potentially reduce POM formation and emissions. One drawback to the UOP process is that due to its higher temperatures, special materials of construction are required, thus making it more suitable for new cracking units as opposed to existing units. The Amoco process, however, is based on improving the catalytic reactor efficiency and allowing more complete combustion to occur in the catalyst regenerator without having to operate at higher temperatures. Because changes in basic equipment are minimal with the Amoco process, it is more amenable for retrofitting existing units (Radian, 1980).

#### Emission Factors

Emission factors for the catalyst regenerator portion of fluidized- and moving-bed catalytic cracking units are presented in Table 4.5-1 (Hangebrauck et al., 1967). As indicated by the date of the reference, POM emission data from catalytic cracking have not been updated since Hangebrauck summarized these emission factors. The only newer data that are available for POM from catalytic cracking are those for naphthalene emissions (Radian, 1991).

The emission factors that were reported by Hangebrauck et al. (1967) for all FCC, TCC, and HCC units exhibit a large amount of variability. In uncontrolled FCC units, pyrene, phenanthrene, and fluoranthene were the predominant compounds measured. Perylene, anthracene, and coronene were not detected in uncontrolled emissions from the FCC unit. Benzo(a)pyrene levels were found to be relatively minor (average of  $3.74 \times 10^{-6}$  lb [ $1.69 \times 10^{-7}$  kg] per barrel of oil feed versus an average of  $2.94 \times 10^{-4}$  lb [ $1.33 \times 10^{-4}$  kg] per barrel of oil feed for phenanthrene; a standard barrel of oil contains 42 gallons [160 liters]). The positive effect of CO waste heat boilers as control devices for FCC unit regenerator flue gases can also be seen (Hangebrauck et al., 1967).

Emissions of PAH were highest in general from the controlled TCC unit (air lift type) and the uncontrolled HCC unit. In the air lift TCC unit, pyrene, phenanthrene, benzo(ghi)perylene, and benzo(a)pyrene emission levels were the highest of the ten PAH measured. Similarly, benzo(ghi)perylene, benzo(e)pyrene, pyrene, and benzo(a)pyrene were the most significant compounds measured in uncontrolled HCC unit emissions. Both types of TCC units were equipped with plume burners. The data for the HCC unit suggests the effectiveness of venting regenerator emissions to CO waste heat boilers for PAH emission control. For each of the ten PAH compounds measured, the CO waste heat boiler reduced uncontrolled HCC regenerator emissions by greater than 99 percent.

Data obtained to support the development of the Petroleum Refinery NESHAP was used to calculate an emission factor for naphthalene from an FCC unit without a CO waste heat boiler (i.e., uncontrolled) (Radian, 1991). This emission factor, which is presented in Table 4.5-1, is based on information provided by only one refinery and may not be representative of similar units. Data for total POM were also provided in response to the EPA ICR and Section 114 surveys (Radian, 1991). Total annual POM emissions from an uncontrolled catalytic cracking unit were calculated to be 0.0041 lb (0.0018 kg) per barrel of oil charged, which is similar in value to the emission factor for naphthalene. Again, these data are not necessarily representative of the industry as a whole, but they give some small indication of the level of POM emissions that can be expected from today's catalytic cracking units.

TABLE 4.5-1. PAH EMISSION FACTORS FOR PETROLEUM CATALYTIC CRACKING  
CATALYST REGENERATION UNITS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/barrel <sup>a</sup> (kg/barrel)	Emission Factor Rating	Reference
3-06-002-01	Fluid Catalytic Cracking Unit	Uncontrolled	Benzo(a)pyrene	3.7E-07 (1.7E-07)	D	Hangebrauck et al., 1967
			Anthracene	<1.5E-06 (<6.9E-07)	D	Hangebrauck et al., 1967
			Benzo(ghi)perylene	<3.2E-07 (<1.5E-07)	D	Hangebrauck et al., 1967
			Fluoranthene	1.5E-05 (6.7E-06)	D	Hangebrauck et al., 1967
			Naphthalene	1.3E-06 (6.0E-07)	E	Radian, 1991
			Phenanthrene	<3.0E-04 (<1.3E-04)	D	Hangebrauck et al., 1967
			Pyrene	2.1E-05 (9.4E-06)	D	Hangebrauck et al., 1967
			Benzo(e)pyrene	2.7E-06 (1.2E-06)	D	Hangebrauck et al., 1967
			Benzo(a)pyrene	2.4E-08 (1.1E-08)	D	Hangebrauck et al., 1967
			Benzo(ghi)perylene	4.0E-08 (1.8E-08)	D	Hangebrauck et al., 1967
			Fluoranthene	1.3E-07 (5.9E-08)	D	Hangebrauck et al., 1967
			Pyrene	2.0E-07 (9.2E-08)	D	Hangebrauck et al., 1967
			Benzo(e)pyrene	2.9E-08 (1.3E-08)	D	Hangebrauck et al., 1967

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(continued)



TABLE 4.5-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/barrel <sup>a</sup> (kg/barrel)	Emission Factor Rating	Reference
3-06-003-01	Moving-bed Catalytic Cracking Process - Thermoform (airlift)	Plume Burner	Benzo(a)pyrene	1.8E-04 (7.9E-05)	D	Hangebrauck et al., 1967
			Anthracene	3.3E-06 (1.5E-05)	D	Hangebrauck et al., 1967
			Benzo(ghi)perylene	1.3E-04 (5.7E-05)	D	Hangebrauck et al., 1967
			Fluoranthene	2.9E-05 (1.3E-05)	D	Hangebrauck et al., 1967
			Phenanthrene	5.6E-04 (2.5E-04)	D	Hangebrauck et al., 1967
			Pyrene	4.7E-04 (2.1E-04)	D	Hangebrauck et al., 1967
			Anthanthrene	5.5E-06 (2.5E-06)	D	Hangebrauck et al., 1967
			Benzo(e)pyrene	1.1E-04 (4.8E-05)	D	Hangebrauck et al., 1967
			Coronene	2.7E-07 (1.2E-07)	D	Hangebrauck et al., 1967
			Perylene	1.8E-05 (8.1E-06)	D	Hangebrauck et al., 1967
3-06-003-01	Moving-bed Catalytic Cracking Process - Thermoform (bucket lift)	Plume Burner	Benzo(a)pyrene	3.5E-08 (1.6E-08)	D	Hangebrauck et al., 1967
			Fluoranthene	1.8E-07 (8.3E-08)	D	Hangebrauck et al., 1967
			Pyrene	7.1E-07 (3.2E-07)	D	Hangebrauck et al., 1967

(continued)

TABLE 4.5-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/barrel <sup>a</sup> (kg/barrel)	Emission Factor Rating	Reference
3-06-003-01 (continued)	Moving-bed Catalytic Cracking Process - Thermoform (bucket lift) (continued)	Plume Burner (continued)	Benzo(e)pyrene	9.1E-08 (4.1E-08)	D	Hangebrauck et al., 1967
3-06-003-01	Moving-bed Catalytic Cracking Process - Houdriflow	Uncontrolled	Benzo(a)pyrene	4.8E-04 (2.2E-04)	E	Hangebrauck et al., 1967
			Anthracene	3.2E-06 (1.5E-06)	E	Hangebrauck et al., 1967
			Benzo(ghi)perylene	7.5E-04 (3.4E-04)	E	Hangebrauck et al., 1967
			Fluoranthene	2.2E-05 (9.9E-06)	E	Hangebrauck et al., 1967
			Phenanthrene	5.5E-05 (2.5E-05)	E	Hangebrauck et al., 1967
			Pyrene	2.9E-04 (1.3E-04)	E	Hangebrauck et al., 1967
			Anthanthrene	3.7E-05 (1.7E-05)	E	Hangebrauck et al., 1967
			Benzo(e)pyrene	7.6E-04 (3.5E-04)	E	Hangebrauck et al., 1967
			Coronene	4.1E-05 (1.9E-05)	E	Hangebrauck et al., 1967
			Perylene	7.5E-05 (3.4E-05)	E	Hangebrauck et al., 1967
3-06-003-01	Moving-bed Catalytic Cracking Process - Houdriflow	CO Waste Heat Boiler	Benzo(a)pyrene	1.0E-07 (4.5E-08)	E	Hangebrauck et al., 1967
			Anthracene	1.7E-08 (7.9E-09)	E	Hangebrauck et al., 1967

(continued)

TABLE 4.5-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/barrel <sup>a</sup> (kg/barrel)	Emission Factor Rating	Reference
3-06-003-01 (continued)	Moving-bed Catalytic Cracking Process - Houdrifiow (continued)	CO Waste Heat Boiler (continued)	Benzo(ghi)perylene	2.8E-07 (1.3E-07)	E	Hangebrauck et al., 1967
			Fluoranthene	5.1E-08 (2.3E-08)	E	Hangebrauck et al., 1967
			Phenanthrene	1.8E-07 (8.3E-08)	E	Hangebrauck et al., 1967
			Pyrene	8.6E-08 (3.9E-08)	E	Hangebrauck et al., 1967
			Anthanthrene	7.1E-09 (3.2E-09)	E	Hangebrauck et al., 1967
			Benzo(e)pyrene	2.1E-07 (9.7E-08)	E	Hangebrauck et al., 1967
			Coronene	1.8E-08 (8.0E-09)	E	Hangebrauck et al., 1967
			Perylene	1.1E-08 (4.8E-09)	E	Hangebrauck et al., 1967

<sup>a</sup>Emission factors are expressed in lb (kg) of pollutant per barrel of oil (fresh feed and recycle) charged.

## Source Locations

As of January 1992, there were 192 petroleum refineries in the United States, with a total crude capacity of 15.3 million barrels per calendar day. The majority of refinery capacity (54 percent) was located in Texas, Louisiana, and California. Other regions with significant refinery capacities were the Chicago, Philadelphia, and Puget Sound areas. Only about two-thirds of these refineries operate catalytic crackers.

### 4.5.2 Other Petroleum Refinery Sources

#### Process Description

The recent MACT standard development effort has indicated the possibility of other minor POM sources in petroleum refineries. Some refineries reported that naphthalene was emitted from process vents on the sulfur recovery, thermal coking, and blowdown systems, and points in the wastewater treatment system. The first three processes may generate POM or may simply emit POM such as naphthalene that are already present in the material being processed. Because these are minor sources and little data are available, the processes are not described. Consult the references should be for more detail.

#### Emission Factors

Even though a few refineries reported that naphthalene was present, emission factors could be developed only for two points in the wastewater treatment process: the oil-water separator and biotreatment. Naphthalene emissions from an oil-water separator were calculated to be on average 1.45 lb (0.65 kg) per million gallons of refinery wastewater treated. An average factor for naphthalene emissions from a biotreatment unit was calculated as 0.565 lb (0.255 kg) per million gallons of refinery wastewater treated. As with the naphthalene emission factor for an uncontrolled FCC unit, it must be emphasized that these data are from a limited number of facilities. No claim is made that these are representative values; rather, they are the only data

available and serve only to give some indication of the type of refinery processes that may generate POM.

The process vent provisions included in the Petroleum Refinery NESHAP affect organic HAP emissions from miscellaneous process vents throughout a refinery. For miscellaneous process vents, the most reported controls were flares, incinerators, and/or boilers. Other controls for miscellaneous process vents reported by refineries include scrubbers, ESPs, fabric filter, and cyclones. The wastewater provisions of the Petroleum Refining NESHAP affect wastewater collection and treatment systems emissions as well. Therefore, emissions from these other sources along with catalytic cracking units may be significantly reduced after the Petroleum Refinery NESHAP is fully implemented (Zarate, 1992).

#### Source Locations

As stated previously, there are nearly 200 refineries in the United States. However, not all of them may operate sulfur recovery, thermal coking, or wastewater systems, although as with catalytic cracking, the majority of the refineries have these systems which can potentially emit naphthalene.

## SECTION 4.5 REFERENCES

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