4.6 ASPHALT PRODUCTS

Asphaltic material is obtained toward the end of fractional distillation of crude oil, has two main end-uses: asphalt roofing products and asphalt paving concrete. The manufacturing processes for these two product lines and the emissions associated with their manufacture are described in this section.

4.6.1 Asphalt Roofing Manufacturing

Process Description

The production of asphalt roofing materials is a commonly found industry owing to the widespread usage of the products in the United States. The asphalt roofing industry manufactures asphalt-saturated felt rolls, shingles, roll roofing with mineral granules on the surface, and smooth roll roofing that may contain a small amount of mineral dust or mica on the surface. Most of these products are used in roof construction, but small quantities are used in walls and other building applications (U.S. EPA, 1995).

Asphalt Delivery, Handling, and Storage--The first step in the process of making asphalt roofing products is the delivery, handling, and storing of asphalt flux. Asphalt flux is the term commonly used in this industry for the asphaltic material that is derived from crude oil. The delivery, handling, and storing of asphalt flux at the asphalt roofing plant has been identified as a potential source of organic emissions, including POM.

Asphalt is normally delivered to an asphalt roofing plant in bulk by pipeline, tanker truck, or railcar. Bulk asphalt delivered in liquid form may range in temperature from 200 to 400°F (93 to 204°C), depending on the type of asphalt and local practice (U.S. EPA, 1980; Kelly, 1983; Gerstle, 1974).

With bulk liquid asphalt, the most common method of unloading is to couple a flexible pipe to the tanker and pump the asphalt directly into the appropriate storage tanks. The tanker cover is partially open during the transfer. Because this is a closed system, the only potential sources of emissions are the tanker and the storage tanks. The magnitude of the emissions from the tanker is at least partially dependent on how far the cover is opened.

Another unloading procedure, of which there are numerous variations, is to pump the hot asphalt into a large open funnel that is connected to a surge tank. From the surge tank, the asphalt is pumped directly into storage tanks. Emission sources under the surge tank configuration are the tanker, the interface between the tanker and the surge tank, the surge tank, and the storage tanks. Emissions from these sources are primarily organic particulate. The quantity of emissions depends on the asphalt temperature and on the asphalt characteristics.

After delivery, asphalt flux is usually stored at 124 to 174°F (51 to 79°C), although storage temperatures of up to 450°F (232°C) have been noted. The lower temperatures are usually maintained with steam coils in the tanks. Oil- or gas-fired preheaters are used to maintain the asphalt flux at temperatures above 200°F (93°C) (U.S. EPA, 1980; Kelly, 1983; Gerstle, 1974).

Asphalt flux is usually transferred from storage and around the roofing plant by closed pipeline. Barring leaks, the only potential emissions would come from the end-points of the pipes. These end-points are the storage tanks, the asphalt heaters (if not of the closed-tube type), and the air-blowing stills.

<u>Asphalt Air-Blowing</u>--Before use, asphalt flux must first be converted to either of two roofing grades of asphalt: saturant or coating. Saturant and coating asphalts are primarily distinguished by their softening points. The softening point of saturant asphalts is 104 to 165°F (40 to 74°C); coating asphalts soften at about 230°F (110°C). These softening points are achieved by "blowing" hot asphalt flux, that is, by blowing air through tanks of hot asphalt flux. This blowing process has been identified as a primary source of POM emissions.

The configuration of a typical asphalt air-blowing operation is shown in Figure 4.6.1-1 (U.S. EPA, 1995). This operation consists primarily of a blowing still,

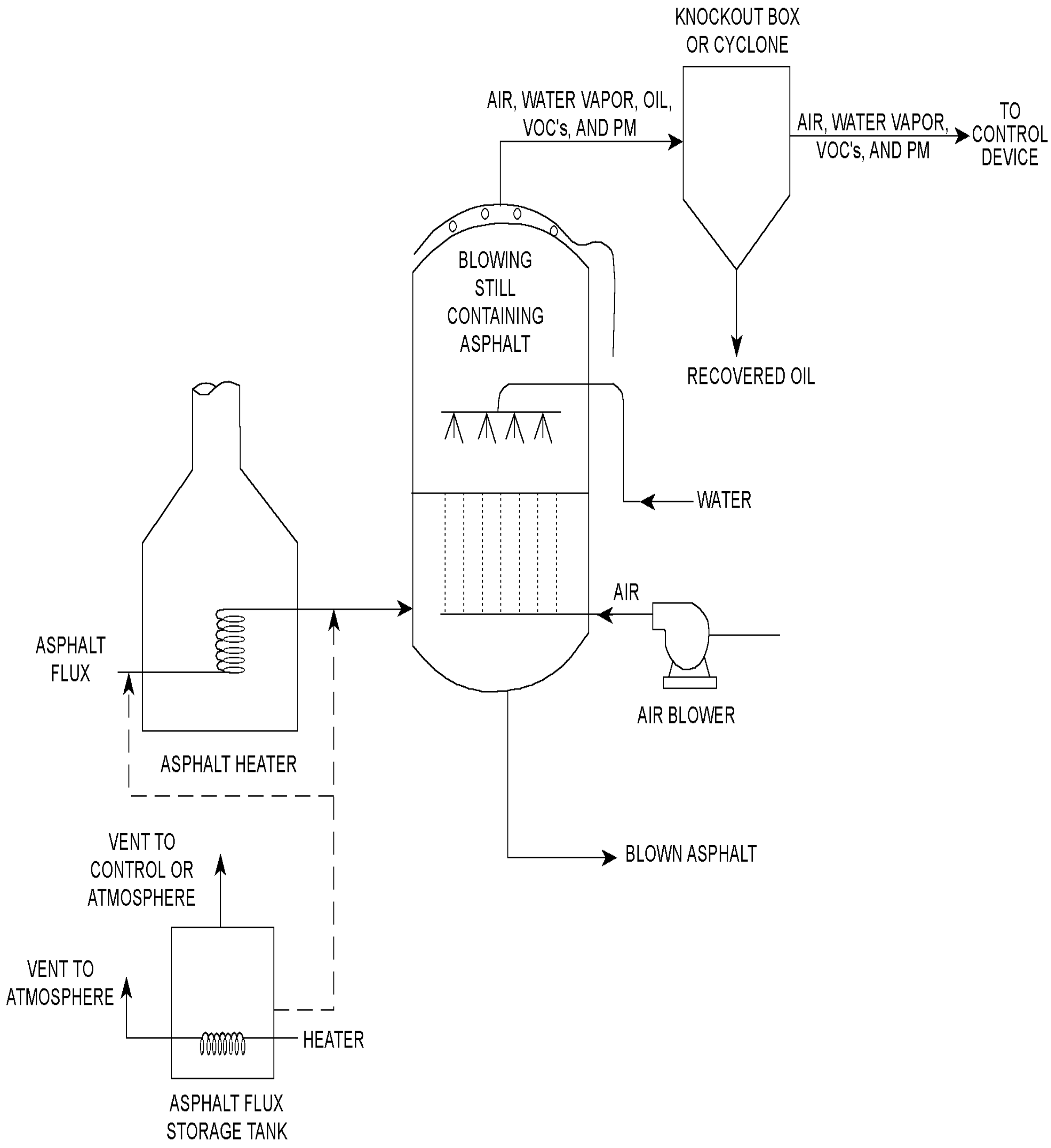


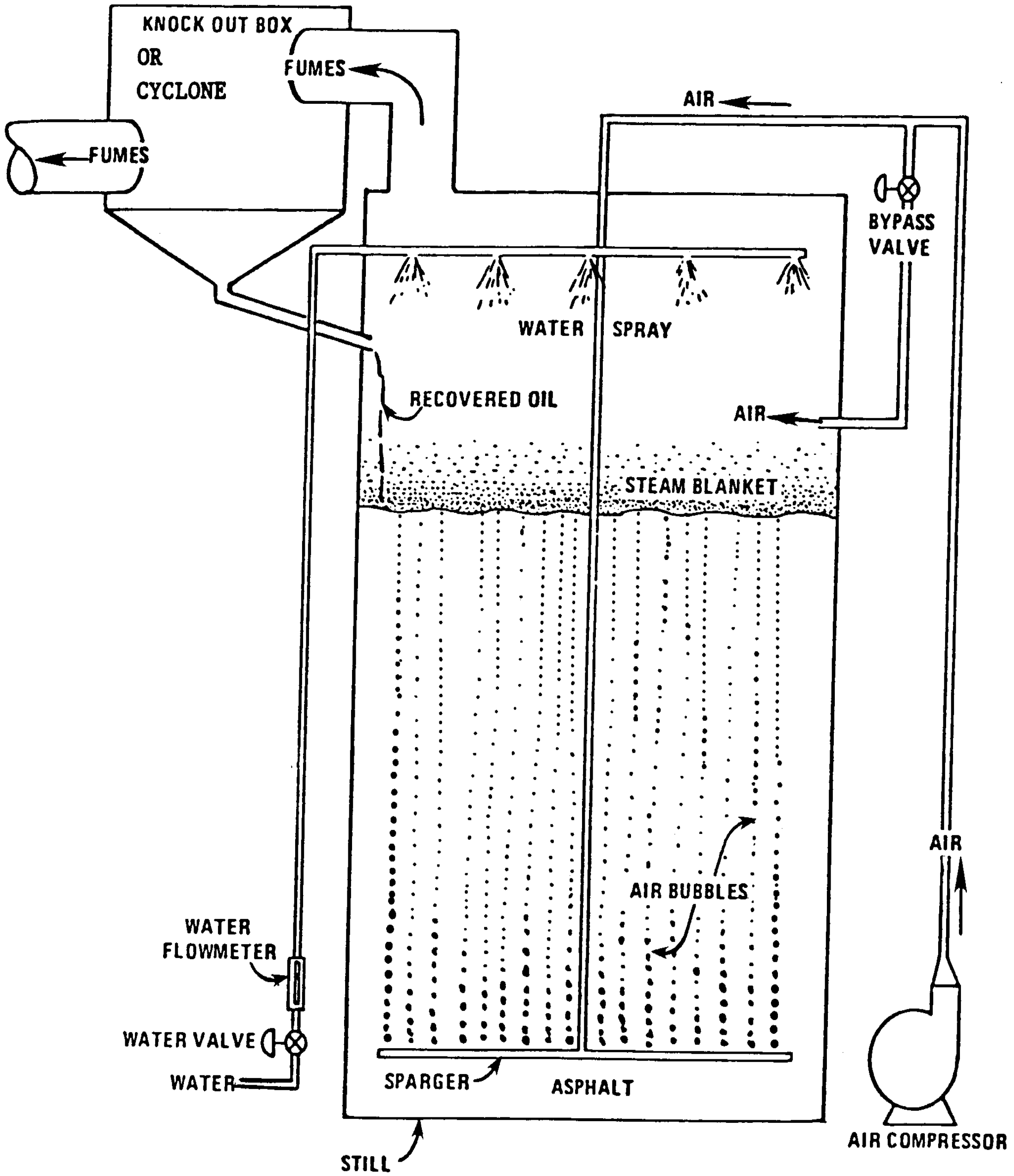
Figure 4.6.1-1. Asphalt Blowing Process Flow Diagram

Source: U.S. EPA, 1995.

which is a tank with a sparger fitted near its base. The purpose of the sparger is to increase contact between the blowing air and the asphalt. Air is forced through holes in the sparger into a tank of hot asphalt flux. The air rises through the asphalt and initiates an exothermic oxidation reaction. Oxidizing the asphalt has the effect of raising the softening temperature, reducing penetration, and modifying other characteristics. Inorganic salts such as ferric chloride ($FeCl_3$) may be used as catalysts added to the asphalt flux during air blowing to facilitate these transformations (U.S. EPA, 1995). The time required for air blowing of asphalt depends on a number of factors, including the characteristics of the asphalt flux, the characteristics desired for the finished product, reaction temperature, type of still used, air injection rate, and the efficiency with which air entering the still is dispersed throughout the asphalt. Blowing times may vary in duration from 30 minutes to 12 hours, with typical times from 1 to 4.5 hours (U.S. EPA, 1980; U.S. EPA, 1995).

Asphalt blowing is a highly temperature-dependent process because the rate of oxidation increases rapidly with increases in temperature. Asphalt is preheated to 400 to 470°F (204 to 243°C) before blowing is initiated to ensure that the oxidation process will start at an acceptable rate. Conversion does take place at lower temperatures, but is much slower. Because of the exothermic nature of the reaction, the temperature of the asphalt rises as blowing proceeds, which, in turn, further increases the reaction rate. Asphalt temperature is normally kept at about 500°F (260°C) during blowing by spraying water onto the surface of the asphalt, although external cooling may also be used to remove the heat of reaction. The allowable upper limit to the reaction temperature is dictated by safety considerations, with the maximum temperature of the asphalt usually kept at least 50°F (28°C) below the flash point of the asphalt being blown (U.S. EPA, 1980).

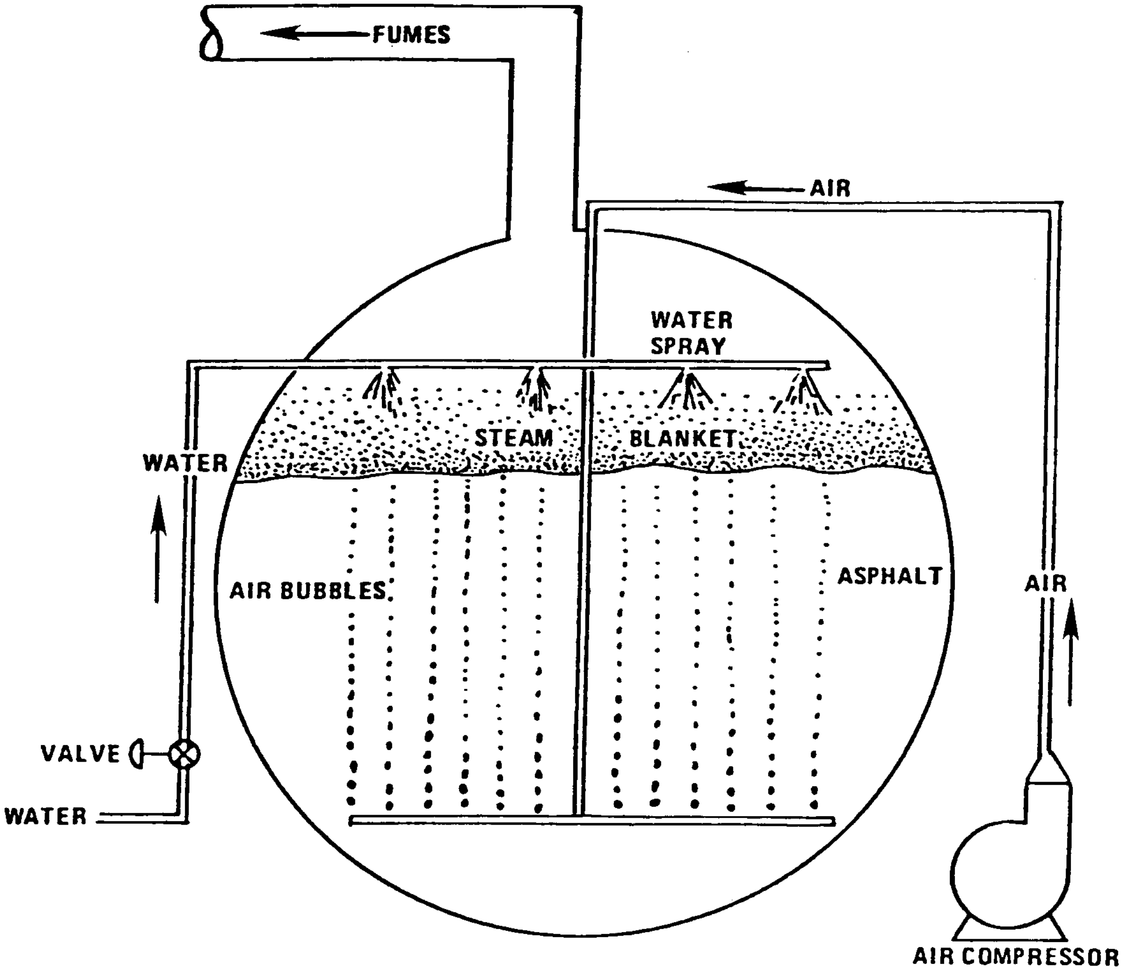
The design and location of the sparger in the blowing still governs how much of the surface area of the asphalt is physically contacted by the injected air, and the vertical height of the still determines the time span of this contact. Vertical stills, because of their greater head (asphalt height), require less air flow for the same amount of asphalt-air contact. Both vertical and horizontal stills (Figure 4.6.1-2 and Figure 4.6.1-3) are used for asphalt blowing, but in new construction, the vertical type is preferred by the industry because of the increased asphalt-air



ERG_POM_4612.pre

Figure 4.6.1-2. Typical Configuration of a Vertical Asphalt Air Blowing Still

Source: U.S. EPA, 1980.



ERG_POM_4613.pre

Figure 4.6.1-3. Typical Configuration of a Horizontal Asphalt Air Blowing Still

Source: U.S. EPA, 1980.

contact and consequent reduction in blowing times (U.S. EPA, 1980). Also, asphalt losses from vertical stills are reported to be less than those from horizontal stills. All recent blowing still installations have been of the vertical type (U.S. EPA, 1995).

Asphalt blowing can be either a batch process or a continuous operation; however, the majority of facilities use a batch process. Asphalt flux is sometimes blown by the oil refiner or asphalt processor to meet the roofing manufacturer’s specifications. Many roofing manufacturers, however, purchase the flux and carry out their own blowing.

<u>Asphalt Saturation</u>--After asphalt has been blown into saturant or coating asphalt, it is used to produce asphalt felt and coated asphalt roofing and siding products in the processes depicted in Figures 4.6.1-4 and 4.6.1-5. The processes are identical to the point at which the material is to be coated. A roll of felt is installed on the felt reel and unwound onto a dry floating looper. The dry floating looper provides a reservoir of felt material to match the intermittent operation of the felt roller to the continuous operation of the line. Felt is unwound from the roll at a faster rate than is required by the line, with the excess being stored in the dry looper. The flow of felt to the line and the tension on the material are kept constant by raising the top set of rollers and increasing looper capacity. The opposite action occurs when a new roll is being put on the felt reel and spliced in, and the felt supply ceases temporarily.

Following the dry looper, the felt enters the saturator, another point of POM emissions within the asphalt roofing process. Moisture is driven out of the felt in the saturator and the felt fibers and intervening spaces are filled with saturant asphalt. If a fiberglass mat web is used instead of felt, the saturation step and the subsequent drying-in process are bypassed. The saturator also contains a looper arrangement, which is almost totally submerged in a tank of asphalt maintained at a temperature of 450 to 500°F (232 to 260°C). The absorbed asphalt increases the sheet or web weight by about 150 percent. At some plants, the felt is sprayed on one side with asphalt to drive out the moisture prior to dipping. This approach reportedly results in higher POM emissions than does use of the dip process alone (U.S. EPA, 1980).

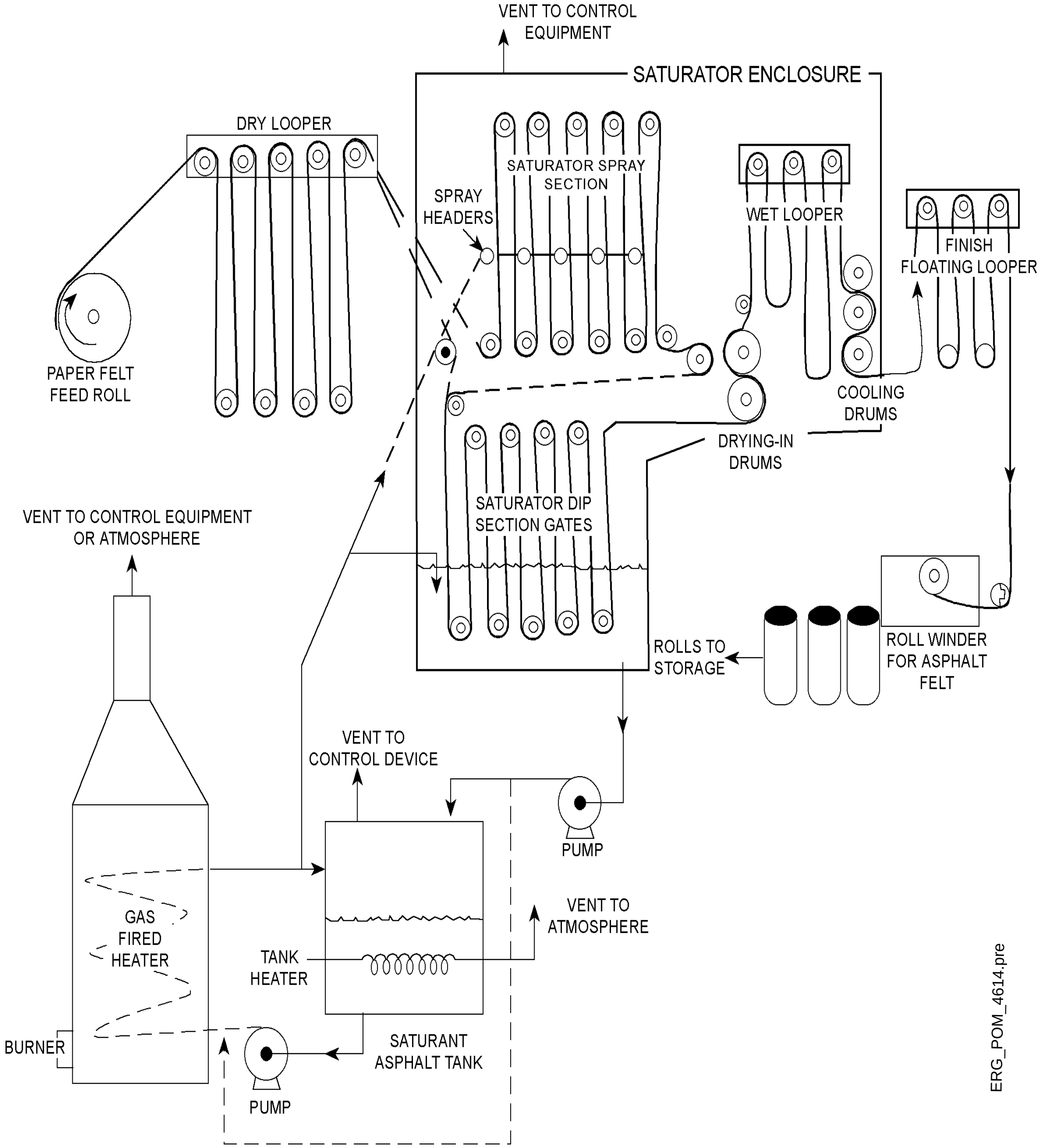


Figure 4.6.1-4. Asphalt-saturated Felt Manufacturing Process

Source: U.S. EPA, 1994.

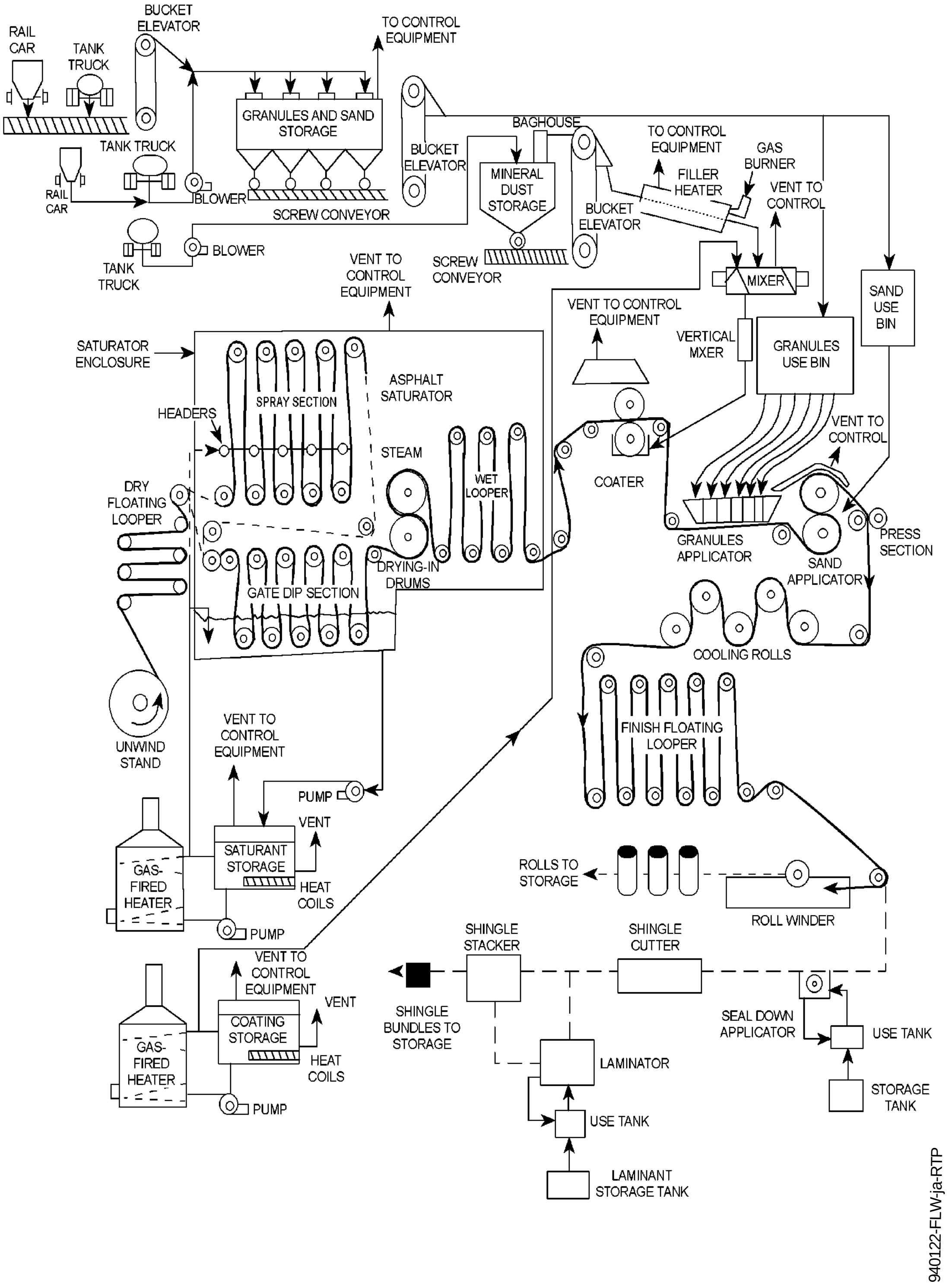


Figure 4.6.1-5. Organic Shingle and Roll Manufacturing Process Flow Diagram

Source: U.S. EPA, 1995.

The saturated felt then passes through drying-in drums and onto the wet looper, sometimes called the hot looper. The drying-in drums press surface saturant into the felt. Depending on the required final product, additional saturant may also be added at this point. The amount of absorption depends on the viscosity of the asphalt and the length of time the asphalt remains fluid. The wet looper increases absorption by providing time for the saturant asphalt to penetrate the felt. The wet looper operation has been shown to be a source of organic particulate emissions within the asphalt roofing process; however, the portion that is POM has not been defined (U.S. EPA, 1980; Kelly, 1983).

<u>Asphalt Coating and Surfacing</u>--If saturated felt is being produced, the sheet passes directly to the cool-down section. For surfaced roofing products, however, the saturated felt is carried to the coater station, where a stabilized asphalt coating is applied to both the top and bottom surfaces. Stabilized coating contains a mineral stabilizer and a harder, more viscous coating asphalt that has a higher softening point than saturant asphalt. The coating asphalt and mineral stabilizer are mixed in approximately equal proportions. The mineral stabilizer may consist of finely divided lime, silica, slate dust, dolomite, or other mineral materials.

The coating asphalt and mineral stabilizer are combined in the coater-mixer. The asphalt is piped into the coater-mixer at about 450 to 500°F (232 to 260°C), and the mineral stabilizer is delivered by screw conveyor. There is often a preheater immediately ahead of the coater-mixer to dry and preheat the material before it is fed into the coater-mixer. This eliminates moisture problems and helps to maintain the temperature above 320°F (160°C). The coater-mixer is usually covered or enclosed, with an exhaust pipe for the air displaced by (or carried with) the incoming materials. The mineral-stabilized coating asphalt is then piped to the coating pan.

The weight of the finished product is controlled by the amount of coating asphalt used. The coater rollers can be moved closer together to reduce the amount of coating applied to the felt, or separated to increase it. Many modern plants are equipped with automatic scales that weigh the sheets in the process of manufacture and warn the coater operator when the product is running under or over specifications.

The next step in the production of coated roofing products is the application of mineral surfacing. The surfacing section of the roofing line usually consists of a multi-compartmented granule hopper, two parting agent hoppers, and two large press rollers. The hoppers are fed through flexible hoses from one or more machine bins above the line. These machine bins provide temporary storage and are sometimes called surge bins. The granule hopper drops colored granules from various compartments onto the top surface of the moving sheet of coated felt in the sequence necessary to produce the desired color pattern on the roofing. This step is not required for smooth-surface products (U.S. EPA, 1980).

Parting agents such as talc and sand (or some combination thereof) are applied to the top and back surfaces of the coated sheet from parting agent hoppers. These hoppers are usually of an open-top, slot-type design, slightly longer than the coated sheet is wide, with a screw arrangement for distributing the parting agent uniformly throughout its length. The first hopper is positioned between the granule hopper and the first large press roller, and 8 to 12 inches. (0.2 to 0.3 m) above the sheet. It drops a generous amount of parting agent onto the top surface of the coated sheet and slightly over each edge. Collectors are often placed at the edges of the sheet to pick up this overspray, which is then recycled to the parting agent machine bin by open screw conveyor and bucket elevator. The second parting agent hopper is located between the rollers and dusts the back side of the coated sheet. Because of the steep angle of the sheet at this point, the average fall distance from the hopper to the sheet is usually somewhat greater than on the top side, and more of the material falls off the sheet (U.S. EPA, 1980).

In a second technique used to apply backing agent to the back side of a coated sheet, a hinged trough holds the backing material against the coated sheet and only material that will adhere to the sheet is picked up. When the roofing line is not operating, the trough is tipped back so that no parting agent will escape past its lower lip.

Immediately after application of the surfacing material, the sheet passes through the cool-down section. Here the sheet is cooled rapidly by passing it around water-cooled rollers in an abbreviated looper arrangement. Usually, water is sprayed on the surfaces of the sheet to speed the cooling process.

Following cooling, self-sealing coated sheets usually have an asphalt seal-down strip applied. The strip is applied by a roller, which is partially submerged in a pan of hot sealant asphalt. The pan is typically covered to minimize fugitive emissions. No seal-down strip is applied to standard shingle or roll goods products. Some products are also texturized at this point by passing the sheet over an embossing roll that forms a pattern in the surface of the coated sheet (U.S. EPA, 1980).

Cooling and Finishing--The cooling process for both asphalt felt and coated sheets is completed in the next processing station, known as the finish looper. In the finish looper, sheets are allowed to cool and dry gradually. Secondly, the finish looper provides line storage to match the continuous operation of the line to the intermittent operation of the roll winder. It also allows time for quick repairs or adjustments to the shingle cutter and stacker during continuous line operation or, conversely, allows cutting and packaging to continue when the line is down for repair. Usually, this part of the process is enclosed to keep the final cooling process from progressing too rapidly. In cold weather, heated air is sometimes used to retard cooling.

Following finishing, asphalt felt to be used in roll goods is wound on a mandrel, cut to the proper length, and packaged. When shingles are being made, the material from the finish looper is fed into the shingle cutting machine. After the shingles have been cut, they are moved by roller conveyor to manual or automatic packaging equipment. They are then stacked on pallets and transferred by fork lift to storage areas or waiting trucks (U.S. EPA, 1980).

As indicated previously, the primary POM emissions sources associated with manufacturing asphalt roofing products are the asphalt air-blowing stills (and associated oil knockout boxes) and the felt saturators (U.S. EPA, 1980). This was determined during development of the NSPS for manufacturing asphalt roofing products. Additional potential POM emission sources include the wet looper, the coater-mixer, the felt coater, the seal-down stripper, and storage tanks for air-blown asphalt. Minor fugitive emissions are also possible from asphalt flux and blown asphalt handling and transfer operations (U.S. EPA, 1980; Kelly, 1983; Gerstle, 1974; Siebert et al., 1978).

Emission Control Techniques--The asphalt roofing products NSPS established limits on particulate emissions and opacity from saturators and blowing operations. Process selection and control of process parameters have been promoted to minimize uncontrolled emissions, including POM, from asphalt air-blowing stills, asphalt saturators, wet loopers, and coaters. Process controls include the use of (U.S. EPA, 1980):

- Dip saturators rather than spray or spray-dip saturators;
- Vertical stills rather than horizontal stills;
- Asphalts that inherently produce low emissions;
- Higher flash point asphalts;
- Reduced temperatures in the asphalt saturant pan;
- Reduced asphalt storage temperatures; and
- Lower asphalt blowing temperatures.

Dip saturators have been installed for most new asphalt roofing line installations in recent years, and this trend is expected to continue. Recent asphalt blowing still installations have been almost exclusively of the vertical type because of the higher efficiency and lower emissions. Vertical stills occupy less space and require no heating during oxidizing (if the temperature of the incoming flux is above 400°F [204°C]). Vertical stills are expected to be used in new installations equipped with stills and in most retrofit situations (U.S. EPA, 1980).

Asphalt fluxes with lower flash points and softening points tend to have higher emissions of organics because these fluxes generally have been less severely cracked and contain more low-boiling fractions. Many of these light ends can be emitted during blowing. Limiting the minimum softening and flash points of asphalt flux should reduce the amount of POM-containing fumes generated during blowing because less blowing is required to produce a saturant or coating asphalt. Saturant and coating asphalts with high softening points should reduce POM emissions from felt saturation and coating operations. However, producing the higher softening asphalt flux requires more blowing, which increases uncontrolled emissions from the blowing operation (U.S. EPA, 1980).

Although these process-oriented emissions control measures are useful, emissions capture equipment and add-on emissions control equipment are also necessary in new asphalt roofing production facilities that are subject to the NSPS. The capture of potential POM emissions from asphalt blowing stills, asphalt storage tanks, asphalt tank truck unloading, and the coater-mixer can be and is being achieved in the industry by the use of enclosure systems around the emissions operations. The enclosures are maintained under negative pressure, and the contained emissions are ducted to control devices (U.S. EPA, 1980). Potential emissions from the saturator, wet looper, and coater are generally collected by a single enclosure, by a canopy type hood, or by an enclosure/hood combination. Typically applied controls for POM emission sources in asphalt roofing plants are summarized in Table 4.6-1.

Emission Factors

Emission factors for POM from asphalt roofing manufacturing are available for asphalt air-blowing stills and saturators (U.S. EPA, 1980). The data were gathered to support development of the NSPS for the asphalt roofing industry, which focused on control of PM and VOC, not individual toxic air pollutants. Because the blowing stills and saturators were identified as significant sources of emissions, the pollutants emitted from these two points in the manufacturing process were characterized more completely than were other emission points. Hence, POM data are available for these two points only, and are presented in Table 4.6-2. Moreover, some POM species were identified in samples, but the amounts present were not or could not be quantified. The POM identified but not quantified are indicated in Table 4.6-2.

Other reports have presented estimates of total POM emissions, both controlled and uncontrolled, from blowing stills, saturators, and other emission points (Gerstle, 1974; Kelly, 1983; Hangebrauck et al., 1967; Siebert et al., 1978). Unfortunately, data are not available to speciate the reported factors into individual POM emission factors. It is worth noting that the reported factors for total POM emissions are highly variable, in part because of differences in

TABLE 4.6-1. CONTROL DEVICES USED ON POM EMISSIONS SOURCES IN ASPHALT ROOFING PLANTS

Emission Source	Control Device
Saturator, wet looper (hot looper), and coater[a]	Afterburner
	High-velocity air filter
	Electrostatic precipitator
Coater-mixer[b]	High-velocity air filter
Asphalt blowing still	Afterburner
Asphalt storage tanks[c]	Mist eliminator

[a] These sources usually share a common enclosure, and emissions are ducted to a common control device.

[b] Emissions from the coater-mixer are controlled at some plants by routing fumes to the control device used for the saturator, wet looper, or coater.

[c] Some plants control emissions from storage tanks with the same device used for processes listed in A and then use a mist eliminator during periods when the roofing line is not operating (e.g., weekends). Asphalt delivery can be accomplished via a closed system that vents emissions to the control device used for the tanks.

Source: U.S. EPA, 1980.

TABLE 4.6-2. PAH EMISSION FACTORS FOR ASPHALT ROOFING MANUFACTURING

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)	Emission Factor Rating
3-05-001-01	Asphalt Blowing: Saturant	Uncontrolled	Anthracene/Phenanthrene	0.0049 (0.0024)[a,b]	D
			Fluoranthene/Methylpyrene	0.0052 (0.0026)[a,b]	D
			Methylanthracenes	0.0134 (0.0067)[a,b]	D
			Methylchrysenes	0.0046 (0.0023)[a,b]	D
3-05-001-01	Asphalt Blowing: Saturant	Afterburner	Anthracene/Phenanthrene	3.3E-05 (1.6E-05)[a,b]	D
			Fluoranthene/Methylpyrene	2.1E-05 (1.1E-05)[a,b]	D
			Methylanthracenes	2.9E-05 (1.4E-05)[a,b]	D
3-05-001-03	Felt Saturation: Dipping Only	Uncontrolled	Anthracene/Phenanthrene	1.2E-04 (6.2E-05)[a,c,d]	D
			Fluoranthene/Methylpyrene	5.3E-05 (2.6E-05)[a,c,d]	D
			Methylanthracenes	3.2E-04 (1.6E-04)[a,c,d]	D
			Methylchrysenes	2.9E-05 (1.5E-05)[a,c,d]	D
3-05-001-03	Felt Saturation: Dipping Only	Afterburner	Benz(a)anthracene/Chrysene	1.1E-04 (5.7E-05)[a,c,e]	D
			Anthracene/Phenanthrene	3.4E-04 (1.7E-04)[a,c,e]	D
			Methylanthracenes	5.7E-04 (2.8E-04)[a,c,e]	D
			Methylchrysenes	1.3E-04 (6.3E-05)[a,c,e]	D

(continued)

TABLE 4.6-2. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)	Emission Factor Rating
3-05-001-03 (continued)	Felt Saturation: Dipping Only	ESP	Anthracene/Phenanthrene	4.8E-05 (2.4E-05)[a,c,e]	D
			Fluoranthene/Methylpyrene	2.3E-05 (1.2E-05)[a,c,e]	D
			Methylanthracenes	1.1E-04 (5.5E-05)[a,c,e]	D

[a] Anthracene, phenanthrene, methylanthracenes, fluoranthene, pyrene, methylpyrene, benz(c)phenanthrene, chrysene, benz(a)anthracene, methylchrysenes, benzofluoranthenes, benzo(a)pyrene, benzo(e)pyrene, and perylene were detected in these emissions, but not all species were quantified.
[b] Emission factors in lb/ton (kg/Mg) of asphalt blown. Factors based on 1 facility.
[c] Emission factors in lb/ton (kg/Mg) of asphalt roofing (e.g., shingles, rolls) produced.
[d] Factors based on 2 facilities.
[e] Factors based on 1 facility.

Source: U.S. EPA, 1980.

sampling and analytical methodology. However, qualitatively the POM compounds identified in the emission streams are very consistent.

The POM compounds identified in roofing source emissions were consistent within a source type (e.g., saturators) and between different source types. Anthracene/ phenanthrene, methyl anthracenes, fluoranthene, pyrene, methyl pyrene, chrysene, benz(a)anthracene, methyl chrysenes, benzofluoranthenes, benzo(a)pyrene, and benzo(e)pyrene were identified in the emissions measurements of practically every source. In both controlled and uncontrolled emissions of saturators and blowing stills, methyl anthracenes predominated. Anthracene/phenanthrene and methyl pyrene/fluoranthene also repeatedly constituted significant portions of total POM emissions. Generally, the three POM compound groups constituted 90 to 95 percent of total POM measured.

Source Locations

A list of all current facilities, as identified by the Asphalt Roofing Manufacturers Association, is provided in Table 4.6-3 (Asphalt Roofing Manufacturers Association, 1994). States containing a relatively significant number of roofing plants include California, Texas, Ohio, and Alabama. These four states contain approximately 40 percent of the total number of roofing facilities. The majority of all plants nationwide are located in urban as opposed to rural areas.

4.6.2 Hot Mix Asphalt Production

Process Description

In the production of hot mix asphalt (also referred to as asphalt concrete), aggregate is heated to eliminate moisture and then mixed with hot asphalt cement. The resulting hot mixture is pliable and able to be compacted and smoothed. When it cools and hardens, hot mix asphalt provides a waterproof and durable pavement for roads, driveways, parking lots, and runways.

TABLE 4.6-3. ASPHALT ROOFING MANUFACTURERS

Company	Roofing Plant Location
Allied-Signal, Inc.	Detroit, MI Fairfield, AL Ironton, OH
Bird, Inc.	Norwood, MA
The Celotex Corporation	Camden, AR Fremont, CA Birmingham, AL Goldsboro, NC Houston, TX Lockland, OH Perth Amboy, NJ San Antonio, TX Los Angeles, CA Memphis, TN
Certainteed Corporation	Shakopee, MN Oxford, NC Milan, OH
Elk Corporation of America	Ennis, TX Tuscaloosa, AL
Fields Corporation	Kent, WA Tacoma, WA
GAF Building Materials, Inc.	Baltimore, MD Dallas, TX Erie, PA Fontana, CA Millis, MA Minneapolis, MN Mobile, AL Mount Vernon, IN Savannah, GA Tampa, FL
Gate Roofing Manufacturing, Inc.	Green Cove Springs, FL
Georgia-Pacific Corporation	Ardmore, OK Daingerfield, TX Franklin, OH Hampton, GA Quakertown, PA

(continued)

TABLE 4.6-3. (Continued)

Company	Roofing Plant Location
Globe Building Materials	Whiting, IN St. Paul, MN Chester, WV
GS Roofing Products Company, Inc.	Charleston, SC Ennis, TX Little Rock, AR Martinez, CA Peachtree City, GA Portland, OR Shreveport, LA Wilmington, CA
Herbert Malarkey Roofing Company	Portland, OR
IKO Chicago, Inc.	Chicago, IL
IKO Production, Inc.	Franklin, OH Wilmington, DE
Koppers Industries, Inc.	Birmingham, AL Chicago, IL Follensbee, WV Houston, TX
Leatherback Industries	Alburquerque, NM Hollister, CA
Lunday-Thagard Company	South Gate, CA
Manville Sales Corporation	Fort Worth, TX Pittsburg, CA Savannah, GA Waukegan, IL
Neste Oil Services	Belton, TX Calexico, CA Fresno, CA Houston, TX Long Beach, CA Pittsburg, CA Salt Lake City, UT San Diego, CA

(continued)

TABLE 4.6-3. (Continued)

Company	Roofing Plant Location
Owens-Corning Fiberglas Corporation	Atlanta, GA Brookville, IN Compton, CA Denver, CO Detroit, MI Houston, TX Irving, TX Jacksonville, FL Jessup, MD Kearny, NJ Medina, OH Memphis, TN Minneapolis, MN Morehead City, NC Oklahoma City, OK Portland, OR
PABCO Roofing Products	Richmond, CA Tacoma, WA
TAMKO Asphalt Products, Inc.	Dallas, TX Frederick, MD Joplin, MO Phillipsburg, KS Tuscaloosa, AL
TARCO, Inc.	North Little Rock, AR Belton, TX
U.S. Intec, Inc.	Corvallis, OR Monroe, GA

Source: Asphalt Roofing Manufacturers Association, 1994.

There are three types of hot mix asphalt plants operating in the United States: batch-mix, continuous-mix, and drum-mix. Batch-mix and continuous-mix plants separate the aggregate drying process from the mixing of aggregate with asphalt cement. Drum-mix plants combine these two processes. Production capacities for all three types of plants range from 40 to 600 tons (36 to 544 Mg) of hot mix per hour. Almost all plants in use are of either the batch-mix or drum-mix type. Less than 0.5 percent of operating hot mix plants are of the continuous-mix design (U.S. EPA, 1995). Over 80 percent of all hot mix asphalt production plants are mobile units (U.S. EPA, 1985).

Aggregate, the basic raw material of hot mix asphalt, consists of any hard, inert mineral material such as gravel, sand, or mineral filler. Aggregate typically comprises 90 to 95 percent by weight of the asphalt mixture. Because aggregate provides most of the load-bearing properties of a pavement, the performance of the pavement depends on selection of the proper aggregate.

Asphalt cement is used as the binding agent for aggregate. It prevents moisture from penetrating the aggregate and acts as a cushioning agent. Typically, asphalt cement constitutes 4 to 6 percent by weight of a hot mix asphalt mixture (U.S. EPA, 1985).

As with the asphalt flux used to produce asphalt roofing products, asphalt cement is obtained from the distillation of crude oil. It is classified into grades under one of three systems. The most commonly used system classifies asphalt cement based on its viscosity at 140°F (60°C). The more viscous the asphalt cement, the higher its numerical rating. An asphalt cement of grade AC-40 is considered a hard asphalt (i.e., a viscosity of 4,000 grams per centimeter per second [g/cm-s or poises]), and an asphalt cement of grade AC-2.5 is considered a soft asphalt (i.e., a viscosity of 250 g/cm-s [poises]).

Several western states use a second grading system that measures viscosity of the asphalt cement after a standard simulated aging period. This simulated aging period consists of exposure to a temperature of 325°F (163°C) for 5 hours. Viscosity is measured at 140°F

(60°C), with grades ranging from AR-1000 for a soft asphalt cement (1000 g/cm-s [poises]) to AR-16000 for a hard asphalt cement (16,000 g/cm-s [poises]).

A third grading system is based on the penetration allowed by the asphalt cement. Grade designation 40 to 50 means that a needle with a weight attached will penetrate the asphalt cement 40 to 50 tenths of a millimeter under standard test conditions. The hard asphalt cements have penetration ratings of 40 to 50, and the soft grades have penetration ratings of 200 to 300 (U.S. EPA, 1985).

The asphalt cement grade selected for different hot mix asphalts depends on the type of pavement, climate, and type and amount of traffic expected. Generally, asphalt pavement bearing heavy traffic in warm climates would require a harder asphalt cement than pavement subject to either light traffic or cold climate conditions.

Another material that is used to a great extent in the production of new or virgin hot mix asphalt is recycled asphalt pavement (RAP), which is pavement material that has been removed from existing roadways. This RAP material is now used by virtually all companies in their hot mix asphalt mixtures. The Surface Transportation Assistance Act of 1982 encourages recycling by providing a 5 percent increase in Federal funds to State agencies that recycle asphalt pavement. Rarely does the RAP comprise more than 60 percent by weight of the new asphalt mixture. Twenty-five percent RAP is typical in batch plants, and 40 to 50 percent RAP mixtures are typical in drum-mix plants (U.S. EPA, 1985).

Rejuvenating agents are sometimes used in hot mix asphalts using RAP to bring the weathered and aged asphalt cement in the recycled mixture up to the specifications of the new asphalt mixture. Usually, soft asphalt cement, specially prepared high-viscosity oil, or hard asphalt cement blended with a low-viscosity oil are used as rejuvenating agents. The amount of rejuvenating agent added depends on the properties of the RAP and the specifications for the hot mix asphalt product.

Sulfur has also been used on an experimental basis as a substitute for a portion of the asphalt cement in hot mix asphalt mixtures. Asphalt cement/sulfur combination is better able to bind with aggregate than is asphalt cement alone. Hot mix asphalt pavements containing the asphalt cement/sulfur combination appear to be stronger and less susceptible to temperature changes than those containing asphalt cement alone.

The use of sulfur is not competitive with asphalt cement in hot mix asphalt mixes for several reasons, including environmental issues, worker objections (odor), and corrosion, all of which result from emissions of hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and elemental sulfur (S). In addition, sulfur is almost twice as dense as asphalt cement. Consequently, to make the use of sulfur economically feasible, the cost of sulfur must be less than half the cost of asphalt cement (U.S. EPA, 1985).

<u>Batch-Mix Process</u>--The primary processes of a typical batch-mix hot mix asphalt facility are illustrated in Figure 4.6.2-1. Aggregate of various sizes is stockpiled at the plant for easy access. Aggregate is typically transported by front-end loader to separate cold feed bins and metered onto a feeder conveyor belt through gates at the bottom of the bins. The aggregate is screened before it is fed to the dryer to keep oversized material out of the mix.

The screened aggregate is then fed to a rotating dryer with a burner at its lower (discharge) end that is fired with fuel oil, natural gas, or propane. The dryer removes moisture from the aggregate and heats the aggregate to the proper mix temperature. Inside the dryer are longitudinal flights (metal slats) that lift and tumble the aggregate, causing a curtain of material to be exposed to the heated gas stream. This curtain of material provides greater heat transfer to the aggregate than would occur if the aggregate tumbled along the bottom of the drum towards the discharge end. Aggregate temperature at the discharge end of the dryer is about 300°F (149°C). The amount of aggregate that a dryer can heat depends on the size of the drum, the size of the burner, and the moisture content of the aggregate. As the amount of moisture to be removed from the aggregate increases, the effective production capacity of the dryer decreases.

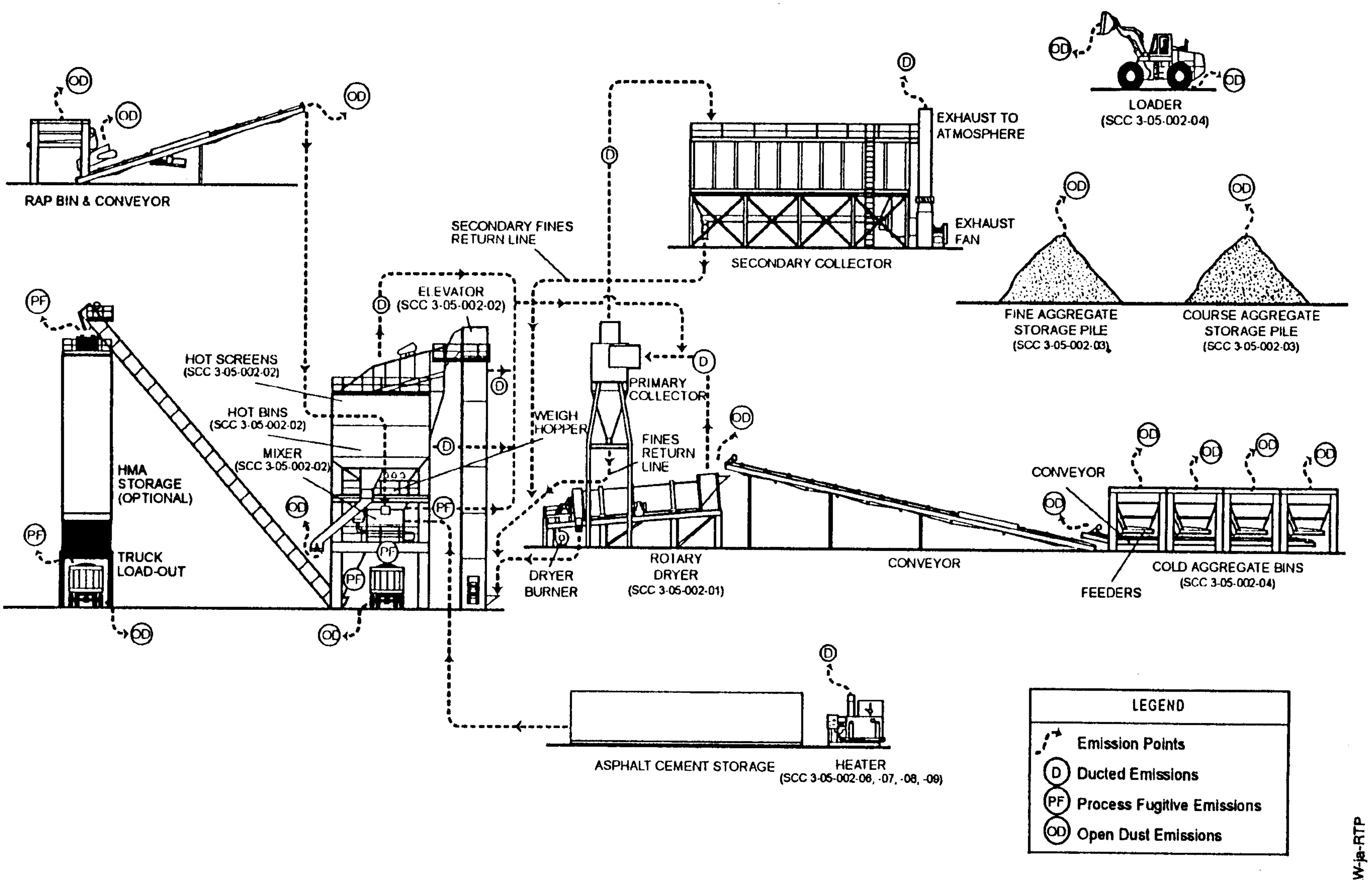


Figure 4.6.2-1. General Process Flow Diagram for Batch Mix Asphalt Paving Plants

Source: U.S. EPA, 1995.

Vibrating screens segregate the heated aggregate into bins according to size. A weigh hopper meters the desired amount of the various sizes of aggregate into a pugmill mixer. The pugmill typically mixes the aggregate for 15 seconds before hot asphalt cement from a heated tank is sprayed into the pugmill. The pugmill thoroughly mixes the aggregate and hot asphalt cement for 25 to 60 seconds. The finished hot mix asphalt is either directly loaded into trucks or held in insulated and/or heated storage silos. Depending on the production specifications, the temperature of the hot mix asphalt product mix can range from 225 to 350°F (107 to 177°C) at the end of the production process.

When a hot mix containing RAP is produced, the aggregate is superheated (compared to totally virgin hot mix asphalt production) to about 600°F (315°C) to ensure sufficient heat transfer to the RAP when it is mixed with the virgin materials. The RAP material may be added either to the pugmill mixer or at the discharge end of the dryer. Rarely is more than 30 percent RAP used in batch plants for the production of hot mix asphalt.

<u>Continuous-Mix Process</u>--Continuous-mix plants are very similar in configuration to batch plants. Continuous-mix plants have smaller hot bins (for holding the heated aggregate). Little surge capacity is required of these bins because the aggregate is continuously metered and transported to the mixer inlet by a conveyor belt. Asphalt cement is continuously added to the aggregate at the inlet of the mixer. The aggregate and asphalt cement are mixed by the action of rotating paddles while being conveyed through the mixer. An adjustable dam at the outlet end of the mixer regulates the mixing time and also provides some surge capacity. The finished mix is transported by a conveyor belt to either a storage silo or a surge bin (U.S. EPA, 1985).

<u>Drum-Mix Process</u>--Drum-mix plants dry the aggregate and mix it with the asphalt cement in the same drum, eliminating the need for the extra conveyor belt, hot bins and screens, weigh hopper, and pugmill used at batch-mix plants. The drum of a drum-mix plant is much like the dryer of a batch plant, but it typically has more flights to increase veiling of the aggregate and improve overall heat transfer. The burner in a drum-mix plant emits a much bushier flame than does the burner in a batch plant. The bushier flame is designed to provide earlier and greater exposure of

the virgin aggregate to the heat of the flame. This design also protects the asphalt cement, which is injected away from the direct heat of the flame (U.S. EPA, 1985).

Initially, drum-mix plants were designed to be parallel flow, as depicted in Figure 4.6.2-2. Recently, the counterflow drum mix plant design shown in Figure 4.6.2-3 has become popular. The parallel flow drum-mix process is a continuous-mixing type process using proportioning cold-feed controls for the process materials. Aggregate, which has been proportioned by gradations, is introduced to the drum at the burner end. As the drum rotates, the aggregates and the combustion products move in parallel toward the other end of the drum. Liquid asphalt cement flow is controlled by a variable flow pump, which is electronically linked to the virgin aggregate and RAP weigh scales. The asphalt cement, along with any RAP and PM from collectors, is introduced in the mixing zone, midway down the drum in a lower temperature zone. The mixture is discharged at the end of the drum and conveyed to a surge bin or storage silos. The exhaust gases also exit the end of the drum and pass on to the collection system (U.S. EPA, 1995).

In the counterflow drum-mix type plant, the material flow in the drum is opposite or counterflow, to the direction of exhaust gases. In addition, the liquid asphalt cement mixing zone is located behind the burner flame zone so as to remove the materials from direct contact with hot exhaust gases. Liquid asphalt cement flow is controlled by a variable-flow pump and is injected into the mixing zone along with any RAP and PM from primary and secondary collectors (U.S. EPA, 1995).

Parallel flow drum-mixers have an advantage in that mixing in the discharge end of the drum captures a substantial portion of the aggregate dust, therefore lowering the load on the downstream collection equipment. For this reason, most parallel-flow drum-mixers are followed only by primary collection equipment (usually a baghouse or venturi scrubber). However, because the mixing of aggregate and liquid asphalt cement occurs in the hot combustion product flow, organic emissions (gaseous and liquid aerosol) from parallel flow drum-mixers may be greater than in other processes (U.S. EPA, 1995).

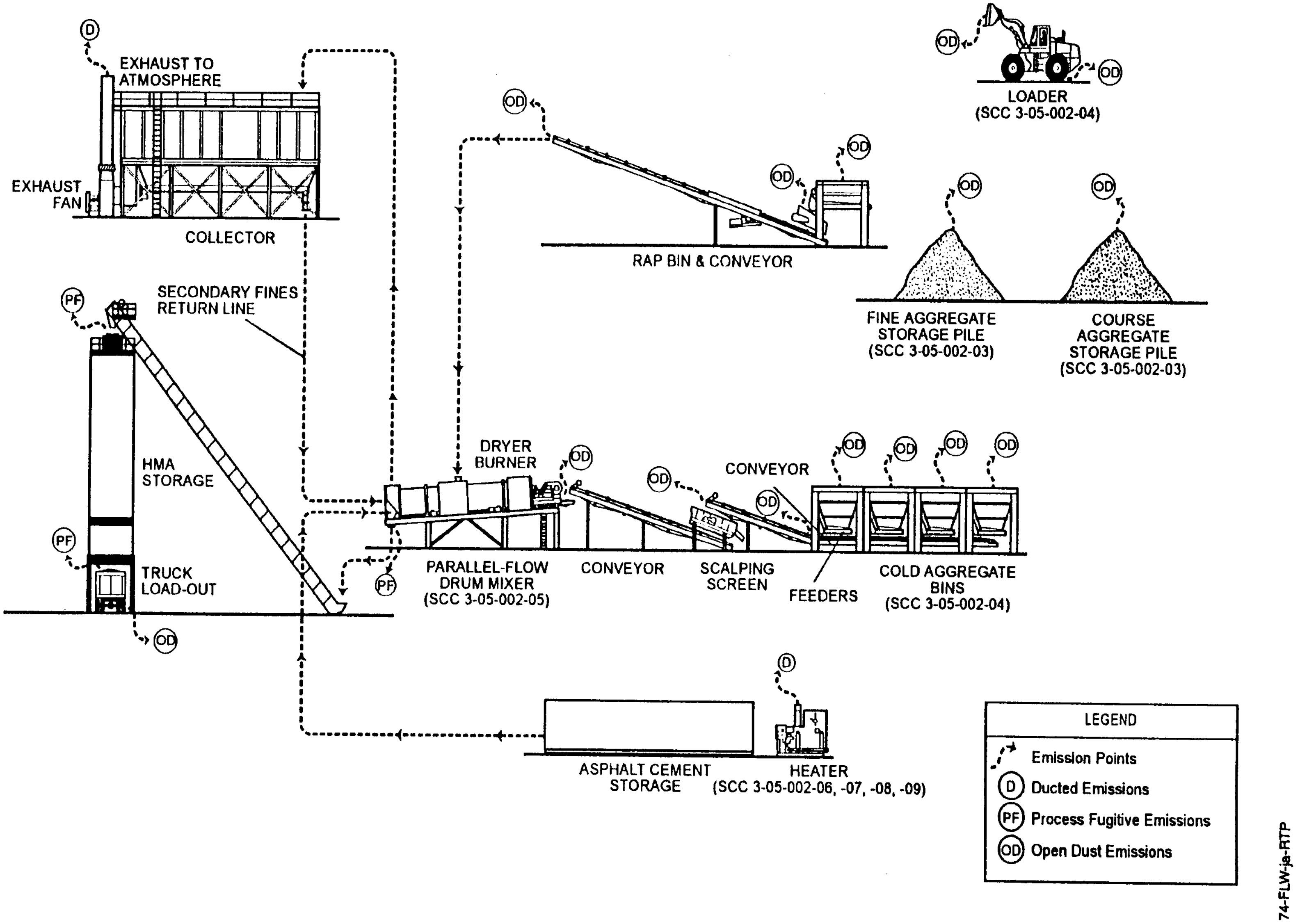


Figure 4.6.2-2. General Process Flow Diagram for Drum Mix Asphalt Paving Plants

Source: U.S. EPA, 1995.

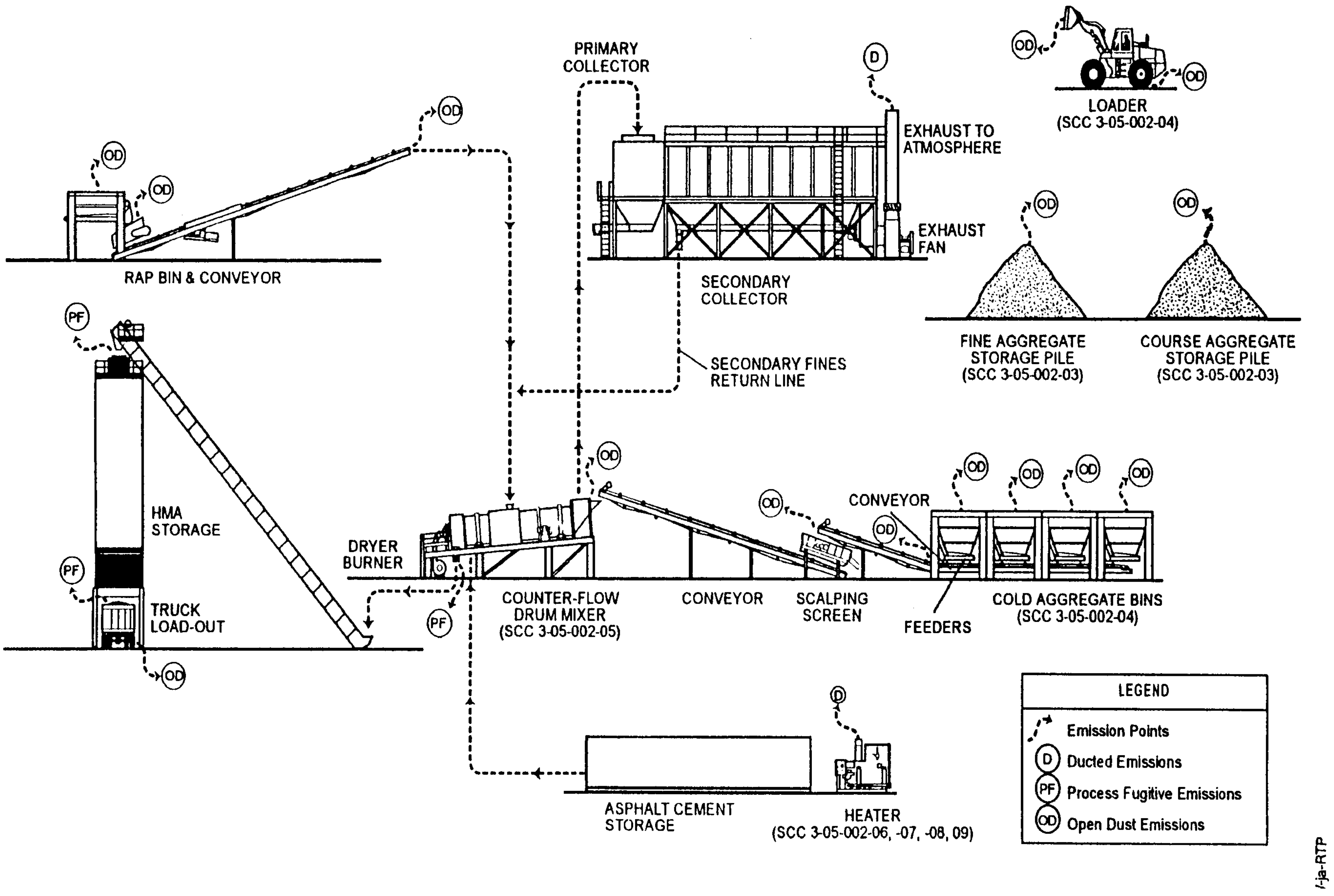


Figure 4.6.2-3. General Process Flow Diagram for Counter-flow Drum Mix Asphalt Paving Plants

Source: U.S. EPA, 1995.

On the other hand, because the liquid asphalt cement, virgin aggregate, and RAP are mixed in a zone removed from the exhaust gas stream, counterflow drum-mix plants will likely have organic emissions (gaseous and liquid aerosol) that are lower than those at parallel flow drum-mix plants. A counterflow drum-mix plant can normally process up to 50 percent RAP with little or no observed effect upon emissions. Today’s counterflow drum-mix plants are designed for improved thermal efficiencies (U.S. EPA, 1995).

Of the 3,600 active hot mix asphalt plants in the United States, approximately 2,300 are batch-mix plants, 1,000 are parallel flow drum-mix plants, and 300 are counterflow drum-mix plants. About 85 percent of plants being manufactured today are of the counterflow drum-mix design; batch-mix plants and parallel flow drum-mix plants account for 10 percent and 5 percent, respectively (U.S. EPA, 1995).

One major advantage of drum-mix plants is that they can produce material containing higher percentages of RAP than can batch-mix plants. The use of RAP significantly reduces the amount of new (virgin) rock and asphalt cement needed to produce hot mix asphalt. With the greater veiling of aggregate, drum-mix plants are more efficient than batch-mix plants at transferring heat and achieving proper mixing of recycled asphalt and virgin materials (U.S. EPA, 1985).

Emission Control Techniques--Emissions of POM from hot mix asphalt plants occur from the aggregate rotary dryers (due to fuel combustion) and from the hot mix asphalt mixing vessels (due to heating of the asphalt materials containing organics). Most plants employ some form of mechanical collection, typically cyclones, to collect aggregate particle emissions from the rotary dryers. These cyclones have a minimal collection efficiency for POM compounds because the POM compounds are either in vapor form or predominantly exist on fine particles not captured by the cyclones. In many installations, the recovered aggregate is recycled to the hot mix asphalt process.

Overall, PM emissions from hot mix asphalt mixers are controlled by wet scrubbers or baghouses (U.S. EPA, 1985). Again, the success of these control devices on POM emissions is dependent on the form of the POM (i.e., vapor versus particulate and fine versus coarse particle). In some installations, the exhaust stream of the rotary dryer cyclones is vented to the baghouse or scrubber used for mixer emissions control (Khan et al., 1977). One early reference indicated that for hot mix asphalt plants venting dry emissions to the mixer control device, the POM compounds detected in the mixer control device emissions were predominantly a function of the rotary dryer and not the mixer (Hangebrauck et al., 1967). Subsequent investigations have not challenged this finding.

In any of the processes used to produce hot mix asphalt, fugitive POM emissions may occur because of evaporative losses from asphalt handling and storage. Emissions of this type would be highly variable. No examination of fugitive POM emissions from hot mix asphalt plants could be found in the literature.

Emission Factors

Emissions from hot mix asphalt plants were reexamined recently for the purpose of updating the information contained in EPA's *Compilation of Air Pollutant Emission Factors,* commonly referred to as AP-42. Representative batch-mix and drum-mix plants (both parallel flow and counterflow) were selected for testing. Emissions from hot oil heaters used to warm stored asphalt concrete were also evaluated. Process emissions from hot mix plants include criteria pollutants (i.e., PM, CO, CO_2, NO_x, SO_2, and VOC) as a result of fuel combustion, aggregate mixing and drying, and asphalt heating. Metal emissions are also of concern. POM emissions are associated both with VOC and PM. The POM emission factors that were developed for this AP-42 revision are provided in Tables 4.6-4, 4.6-5, and 4.6-6 (U.S. EPA, 1995).

Previously, it had been thought that batch-mix plants tended to have a lower level of total POM emissions than drum-mix plants (U.S. EPA, 1980). Such a conclusion cannot be found in the more recent data. On the other hand, the newer reports indicate that counterflow drum-mix plants can be expected to emit smaller quantities of organic compounds than parallel

TABLE 4.6-4. PAH EMISSION FACTORS FOR BATCH-MIX HOT MIX ASPHALT PLANTS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-05-002-01	Natural Gas-fired Dryer	Fabric Filter	Benz(a)anthracene	4.5E-09 (2.3E-09)	D
			Benzo(b)fluoranthene	4.5E-09 (2.3E-09)	D
			Benzo(k)fluoranthene	2.4E-08 (1.2E-08)	E
			Chrysene	6.1E-09 (3.1E-09)	D
			Acenaphthene	1.2E-06 (6.2E-07)	D
			Acenaphthylene	8.6E-07 (4.3E-07)	D
			Anthracene	3.1E-07 (1.5E-07)	D
			Fluoranthene	3.1E-07 (1.6E-07)	D
			Fluorene	2E-06 (9.8E-07)	D
			Naphthalene	4.2E-05 (2.1E-05)	D
			Phenanthrene	3.3E-06 (1.6E-06)	D

(continued)

TABLE 4.6-4. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-05-002-01 (continued)	Natural Gas-fired Dryer (continued)	Fabric Filter (continued)	Pyrene	6.2E-08 (3.1E-08)	D
			2-Methylnaphthalene	7.7E-05 (3.8E-05)	D
3-05-002-01	Oil-fired Dryer	Fabric Filter	Fluoranthene	2.4E-05 (1.2E-05)	D
			Naphthalene	4.5E-05 (2.2E-05)	D
			Phenanthrene	3.7E-05 (1.8E-05)	E
			Pyrene	5.5E-05 (2.7E-05)	D
			2-Methylnaphthalene	6E-05 (3E-05)	D

[a] Emission factors in lb/ton (kg/Mg) of hot mix asphalt produced.

Source: U.S. EPA, 1995.

TABLE 4.6-5. PAH EMISSION FACTORS FOR DRUM-MIX HOT MIX ASPHALT PLANTS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-05-002-05	Natural Gas- or Propane-fired Dryer	Fabric Filter	Benz(a)anthracene	2.0E-07 (1.0E-07)	D
			Benzo(a)pyrene	9.2E-09 (4.6E-09)	D
			Benzo(b)fluoranthene	1.0E-07 (5.1E-08)	D
			Benzo(k)fluoranthene	5.3E-08 (2.6E-08)	D
			Chrysene	3.5E-07 (1.8E-07)	D
			Dibenz(a,h)anthracene	2.7E-09 (1.3E-09)	E
			Indeno(1,2,3-cd)pyrene	7.3E-09 (3.6E-09)	D
			Acenaphthene	1.3E-06 (6.4E-07)	D
			Acenaphthylene	8.4E-06 (4.2E-06)	D
			Anthracene	2.1E-07 (1.0E-07)	D
			Benzo(g,h,i)perylene	3.9E-08 (1.9E-08)	D
			Fluoranthene	5.9E-07 (3.0E-07)	D
			Fluorene	5.3E-06 (2.7E-06)	D
			Naphthalene	4.8E-05 (2.4E-05)	D

(continued)

TABLE 4.6-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-05-002-05 (continued)	Natural Gas- or Propane-fired Dryer (continued)	Fabric Filter (continued)	Phenanthrene	8.4E-06 (4.2E-06)	D
			Pyrene	4.6E-07 (2.3E-07)	D
			2-Chloronaphthalene	1.8E-06 (8.9E-07)	D
			2-Methylnaphthalene	7.4E-05 (3.7E-05	D
			Benzo(e)pyrene	1.0E-07 (5.2E-08)	D
			Perylene	1.2E-08 (6.2E-09)	E
3-05-002-05	Oil-fired Dryer	Fabric Filter	Acenaphthylene	2.2E-05 (1.1E-05)	D
			Anthracene	3.6E-06 (1.8E-06)	D
			Fluorene	1.7E-05 (8.5E-06)	D
			Naphthalene	3.1E-04 (1.6E-04)	D
			Phenanthrene	5.5E-05 (2.8E-05)	D
			Pyrene	3.0E-06 (1.5E-06)	E
			2-Methylnaphthalene	1.7E-04 (8.5E-05)	D

[a] Emission factors in lb/ton (kg/Mg) of hot mix asphalt produced. Includes data from both parallel flow and counterflow dryers.

Source: U.S. EPA, 1995.

TABLE 4.6-6. PAH EMISSION FACTORS FOR HOT MIX ASPHALT HOT OIL HEATERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/gal (kg/l)[a]	Emission Factor Rating
3-05-002-08	Hot Oil Heater, No. 2 Fuel Oil	Uncontrolled	Benzo(b)fluoranthene	1.0E-07 (1.2E-08)	E
			Acenaphthene	5.3E-07 (6.4E-08)	E
			Acenaphthylene	2.0E-07 (2.4E-08)	E
			Anthracene	1.8E-07 (2.2E-08)	E
			Fluoranthene	4.4E-08 (5.3E-09)	E
			Fluorene	3.2E-08 (3.8E-09)	E
			Naphthalene	1.7E-05 (2E-06)	E
			Phenanthrene	4.9E-06 (5.9E-07)	E
			Pyrene	3.2E-08 (3.8E-09)	E

[a] Emission factors in lb/gal (kg/l) of fuel consumed. Includes data from both parallel flow and counterflow dryers.

Source: U.S. EPA, 1995.

flow plants. However, the available data are insufficient to accurately quantify the difference (U.S. EPA, 1995).

The potential effect of the type of fuel used in the dryer, natural gas versus oil, can be seen in the data in Table 4.6-5. Results from older tests are also presented (Fuchs et al., 1984; Khan et al., 1977). These emission factors from older tests do not specify the fuel used in the dryers; however, they indicate the potential effect different types of control devices may have on emissions from drum-mix versus batch-mix plants.

The older tests also focused on the state in which the POM species exist when emitted (i.e., the vapor phase or solid particulate). The data indicate that drum-mix plants emit POM primarily in the vapor phase, whereas POM is emitted mainly as PM from batch-mix plants. The more recent testing did not attempt to confirm the findings regarding vapor phase versus particulate POM emissions, but there is no indication that the results are no longer true. Hence, it would seem that PM control techniques are not entirely suitable for controlling POM from drum-mix plants, or that a combination of techniques to control both vapor phase and solid emissions is called for at hot mix asphalt plants.

Source Locations

In 1983, there were approximately 2,150 companies operating an estimated 4,500 hot mix asphalt plants in the United States (U.S. EPA, 1985). Today, the number has fallen to approximately 3,600 plants (U.S. EPA, 1995). Approximately 40 percent of these companies operate only a single plant. Because plants must be located near the job site, plants are concentrated in areas where the highway and road network is concentrated (U.S. EPA, 1985). Additional information on the locations of individual hot mix asphalt facilities can best be obtained by contacting the National Asphalt Pavement Association in Lanham, Maryland.

SECTION 4.6 REFERENCES

Asphalt Roofing Manufacturers Association, letter to E. Paik, Radian Corporation. List of Member Asphalt Roofing Manufacturing Plants and Locations. August 22, 1994.

Fuchs, M.R. et al. Emission Test Report: T.J. Campbell Asphalt Concrete Plant, Oklahoma City, Oklahoma. U.S. Environmental Protection Agency, Emissions Measurement Branch, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA/EMB Report No. 83-ASP-4. May 1984.

Gerstle, R.W. Atmospheric Emissions From Asphalt Roofing Processes. U.S. Environmental Protection Agency, Control Systems Laboratory, Research Triangle Park, North Carolina. EPA-650/2-74-101. October 1974.

Hangebrauck, R.P. et al. Sources of Polynuclear Hydrocarbons in the Atmosphere. Public Health Service, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio. Public Health Service Report No. AP-33. pp. 27-28. 1967.

Kelly, M.E. Sources and Emissions of Polycyclic Organic Matter. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA-450/5-83-010b. pp. 5-62 to 5-68. 1983.

Khan, Z.X. et al. “Polycyclic Organic Material Emissions from Asphalt Hot Mix Plants.” Paper presented at the 70th Annual Meeting of the Air Pollution Control Association, Toronto, Ontario, Canada. Paper No. 77-16.4. June 20-24, 1977.

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). Prepared for U.S. Environmental Protection Agency, Pollutant Strategies Branch, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA Contract No. 68-02-2836. pp. 72-78. November 1978.

U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. Volume I: Stationary Point and Area Sources. AP-42, Fifth Edition. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. pp. 11.1-1 to 11.1-5 and 11.2-1 to 11.2-5. 1995.

U.S. Environmental Protection Agency. Second Review of NSPS for Asphalt Concrete Plants. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/3-85-024. October 1985.

U.S. Environmental Protection Agency. Asphalt Roofing Manufacturing Industry Background Information Document for Proposed Standards. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/3-80-021a. June 1980.

4.7 COKE PRODUCTION

The coke production source category consists of the processes used to produce coke from coal and the recovery and treatment of byproduct gases from the coking process to generate secondary products such as crude tars, light oil, and ammonia.

Metallurgical coke is used in iron and steel industry processes (primarily in blast furnaces) to reduce iron ore to iron. Over 90 percent of total coke production is dedicated to blast furnace operations. Foundry coke comprises most of the balance and is used in foundry furnaces for melting metal and in the preparation of molds. Foundry coke production uses a different blend of coking coals, longer cooking times, and lower coking temperatures relative to those used for metallurgical coke.

Most coke plants are colocated with iron and steel production facilities, and the demand for coke generally corresponds to the production of iron and steel. There has been a steady decline in the number of coke plants over the past several years for many reasons, including a decline in the demand for iron/steel, increased production of steel by mini-mills (electric arc furnaces that do not use coke), and the lowering of the coke:iron ratio used in the blast furnace (e.g., increased use of pulverized coal injection). There were 28 coke plants operating in the U.S. in 1992. Most coke is produced in the U.S. using the “byproduct” process, and one plant uses a “nonrecovery” process (U.S. EPA, 1995).

The coking industry is classified into two general sectors, furnace plants and merchant producers. Furnace plants are owned by or affiliated with iron- and steel-producing companies that produce coke primarily for consumption in their own blast furnaces, although some furnace plants also engage in intercompany sales with steel firms with excesses or deficits in coke capacity. On the other hand, independent merchant plants produce coke for sale on the open market and are typically owned by chemical and coal firms. These plants sell most of their products to other companies engaged in blast furnace, foundry, and nonferrous smelting operations. In a recent Federal rulemaking, merchant plants are now referred to as “foundry coke producers” (57 FR 57534). In 1984, furnace plants accounted for about 92 percent of the total coke production, and foundry coke producers accounted for the remaining 8 percent, a distribution that has not changed significantly (U.S. EPA, 1987).

Over 10,000 constituents have been identified in coke oven emissions, a yellow-brown gas evolved during coking. These constituents include organic and inorganic particulate matter, VOC, and gases such as H_2S, SO_2, NO_x, NH_3, CO, and others. Many of the volatile components of coke oven gas are identified as HAPs in the 1990 Clean Air Act Amendments. The EPA listed coke oven emissions themselves as a HAP as early as 1984. Because of the variability in composition, the thousands of components of organic particulate matter in coke oven emissions, including POM, have been consolidated for measurement as a single quantity called benzene soluble organic (BSO). The compounds that comprise BSO are high molecular weight organics that can be collected and dissolved in benzene and that remain after the benzene is evaporated off the sample. In general, BSO is composed of compounds having 16 or more carbon atoms. Coke oven gas contains measurable amounts of the POMs listed in Table 4.7-1, and can be emitted from points throughout the entire coking process. The POM and other aromatics in coke oven emissions are a primary health concern and the reason why the coke production source category has been investigated for regulation for more than a decade. Federal rulemakings target the emissions from each of the four main operations in the byproduct coking process: (1) coal preparation and charging, (2) thermal distillation of coal (i.e., coking), (3) handling of the finished coke product, and (4) recovery of coking byproducts. A typical coke oven battery is shown in Figure 4.7-1. A generalized process flow diagram for these operations is shown in Figure 4.7-2 (U.S. EPA, 1987).

The first Federal rule to address coke ovens was a NESHAP promulgated in 1989 targeting the benzene in the emissions from the fourth operation in the coke production cycle, coke byproduct recovery. However, the techniques specified in this standard for controlling benzene emissions also enable the control of the other coke oven gas constituents, namely POM, as well. The next NESHAP to address coke oven emissions was finalized in 1993 and was one of the first standards to be promulgated pursuant to Section 112(d) of the 1990 Clean Air Act. Control of coke oven emissions was explicitly required by the 1990 Clean Air Act Amendments,

TABLE 4.7-1. POM CONSTITUENTS IDENTIFIED IN COKE OVEN GAS

Compound	Percent of BSO[a]
Benz(a)anthracene	1.91
Benzo(a)pyrene	1.38
Benzo(b)fluoranthene	1.71
Benzo(j+k)fluoranthene	1.22
Chrysene/Triphenylene	2.04
Dibenz(a,h)anthracene	0.16
Indeno(1,2,3-cd)pyrene	0.65
Acenaphthene	1.18
Acenaphthylene	5.70
Anthracene	3.42
Benzo(ghi)perylene	0.61
Fluoranthene	6.23
Fluorene	3.91
Naphthalene	20[b]
Phenanthrene	13.6
Pyrene	4.28
1-Methylnaphthalene	3.01
2-Methylnaphthalene	6.76
2-Phenylnaphthalene	0.29
4H-Benzo(def)carbazole	0.29
4H-Cyclopenta(def)chrysene isomers	0.45
4H-Cyclopenta(def)phenanthrene	0.57
Aceanthrylene	0.20
Acephenanthrylene	0.24
Acridine	0.29
Anthanthrene	0.24
Azafluoranthene/Azapyrene	0.04

(continued)

TABLE 4.7-1. (Continued)

Compound	Percent of BSO
Benz(c)acridine	0.33
Benzo(a)fluoranthene	0.33
Benzo(a)fluorene	0.37
Benzo(b)fluorene	0.24
Benzo(c)phenanthrene	0.20
Benzo(e)pyrene	1.30
Benzo(ghi)fluoranthene	0.24
Benzo(b)chrysene	0.08
Benzo(b)naphtho(1,2-d)thiophene	0.24
Benzo(b)naphtho(2,1-d)thiophene	0.57
Benzo(b)naphtho(2,3-d)thiophene	0.24
Benzocarbazoles	0.65
Benzonapthofurans	0.24
Binaphthyls	0.49
Biphenyl	1.51
Carbazole	0.57
Coronene	0.08
Cyclopenta(cd)pyrene	0.12
Dibenz(a,j)anthracene	0.16
Dibenzofuran	5.30
Dibenzothiophene	0.81
Dimethylfluorenes/Trimethyldibenzofurans	0.12
Di- and trimethylnaphthalenes	6.60
Dimethylphenanthrenes/Anthracenes	0.45
Indeno(7,1,2,3-cdef)chrysene	0.16
Methyl- and dimethyldibenzofurans	2.04
Methylacenaphthylenes	1.18

(continued)

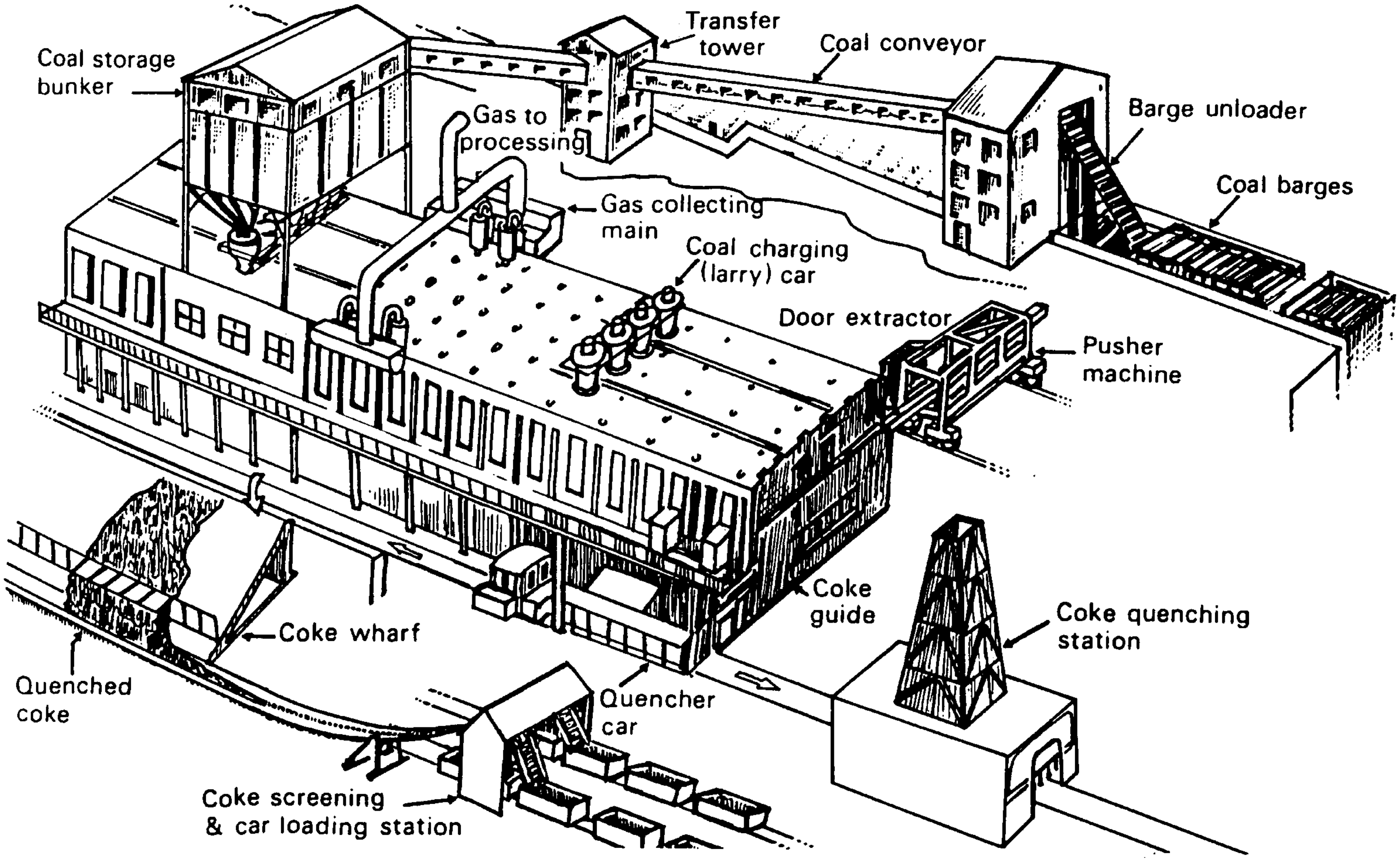
TABLE 4-7.1. (Continued)

Compound	Percent of BSO
Methylbenzfluoranthenes/Methylbenzpyrenes	2.16
Methylbenzfluorenes/Dimethylfluoranthenes/Pyrenes	0.41
Methylbenzoquinolines	0.49
Methylbenzothiophenes	0.41
Methylbinaphthyls	0.37
Methylbiphenyls	1.22
Methylcarbazoles	0.12
Methylchrysenes/Benz(a)anthracenes	0.57
Methylfluoranthenes	0.12
Methylfluorenes	2.81
Methylphenanthrenes/Methylanthracenes	2.28
Methylphenylnaphthalene	0.08
Methylpyrenes	0.12
Naphthoquinolines	0.53
Napthacene	0.37
Perylene	0.37
Phenanthridine	0.45
Phenanthro(4,5-bcd)thiophene	0.29
Picene	0.08
Quinoline	0.20
POM > MW 302	0.94

[a] BSO - Benzene soluble organics.

[b] Naphthalene is not measured as a BSO. The percentage listed reflects the ratio of naphthalene emissions to BSO emissions (0.2:1). (Source: U.S. EPA, 1995).

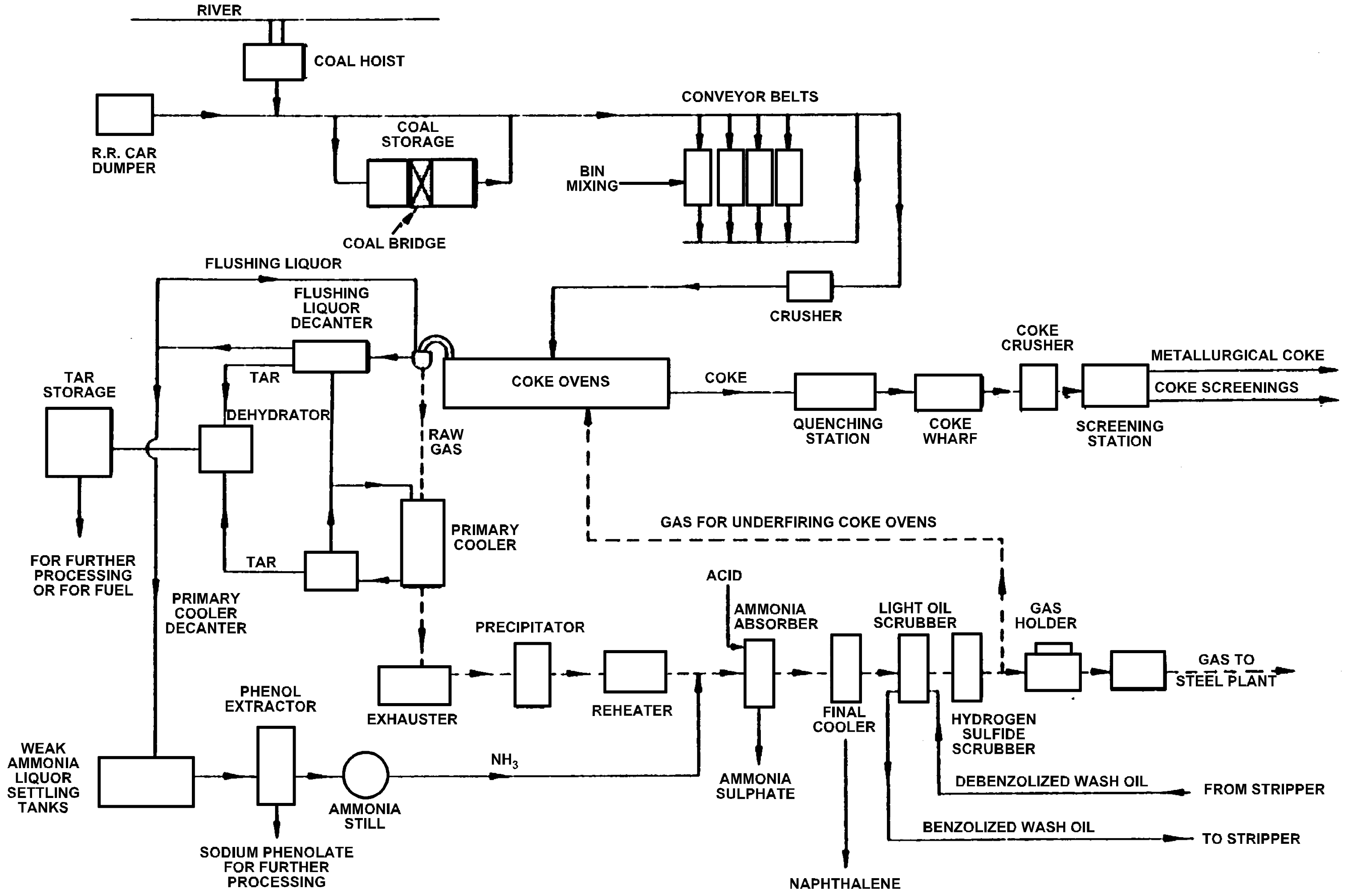
Source: Kirton et al., 1991.



ERG_POM_471.ds4

Figure 4.7-1. View of a Typical Coke Production Plant

Source: IARC, 1984.



ERG_POM_472.ds4

Figure 4.7-2. Flow Sheet Showing the Major Steps in the Byproduct Coking Process

Source: U.S. EPA, 1987.

and the 1993 rule established MACT for coke oven emissions during the initial charging operation and from door and topside leaks during the second operation, coking. A third rule scheduled to be implemented by the year 2000 will address coke oven emissions from the third operation, product handling after the coking cycle is finished, which includes pushing and quenching. This third rule may also target leaks of coke oven gas into combustion stacks during the coking operation, where they can be vented uncontrolled to the atmosphere along with the combustion exhaust. Another MACT standard is also planned for the year 2000 to address the coke byproduct recovery operation again if it is determined that the original 1989 standard needs to be augmented.

Because the 1990, Clean Air Act Amendments specifically required the development of regulations governing coke oven emissions, coke ovens were among the first to be included on the initial list of source categories for which Section 112(d) standards will be developed. Hence, the discussion in this section is organized according to the three MACT standards that have been promulgated or are planned to control coke oven emissions and the POM they contain.

4.7.1 Coke Ovens: Charging, Door and Topside Leaks

Process Description

As shown in Figure 4.7-1, the initial operation in the byproduct coking process is coal preparation and charging. The large majority of POM emissions occur during the charging operation and the subsequent coking operation. Hence, the 1993 MACT standard for coke ovens targeted these two operations and their emission points.

The coal that is charged to a byproduct coke oven is usually a blend of two or more low, medium, or high volatile content coals that are generally low in sulfur and ash. Blending is required to control the properties of the resulting coke and to optimize the quality and quantity of coke byproducts. Blending may also help avoid the expansion exhibited by some types of coal; this expansion may cause excessive pressure on the oven walls during coking and cracking operations, allowing coke oven gas to escape and be emitted from combustion stacks (U.S. EPA, 1987).

Coal is usually received on railroad cars or barges. Conveyor belts transfer the coal as needed from the barges or from a coal storage pile to mixing bins where the various types of coal are stored. The coal is transferred from the mixing bins to a crusher where it is pulverized to a preselected size between 0.006 to 0.13 inch (0.15 to 3.2 mm). The desired size depends on the response of the coal to coking reactions and the ultimate coke strength that is required.

The pulverized coal is then mixed and blended. Sometimes water and oil are added to control the bulk density of the mixture. The prepared coal mixture is transported to coal storage bunkers on the coke oven batteries (a battery is a group of byproduct coke ovens connected by common walls). A weighed amount or volume of prepared coal is discharged from the bunker into a larry car, a vehicle driven by electric motors that travels the length of the battery top on a wide gauge railroad track. The larry car is positioned over the empty, hot oven, the lids on the charging ports are removed, and the coal is discharged from the hoppers of the larry car through discharge chutes. The flow rate from the hoppers to the oven can be controlled by gravity, a rotary table, or screw feeders (U.S. EPA, 1987). To minimize the escape of gases from the oven during charging, steam aspiration is used at most plants to draw gases from the space above the charged coal into the collecting main (U.S. EPA, 1995).

Peaks of coal form directly under the charging ports as the oven is filled. These peaks are leveled by a steel bar that is cantilevered from the pusher machine through an opening called the chuck door on the pusher side of the battery. This leveling process provides a clear vapor space and exit tunnel for the gases that are evolved during coking to flow to the standpipes, which aids the uniform coking of the coal. After filling, the chuck door and the topside charging ports are closed (U.S. EPA, 1987).

The next step in the process is the thermal distillation (i.e., coking) of coal in which volatile components are driven off, leaving a strong matrix of the nonvolatile, high-carbon components that is termed coke. Coking takes place in coke oven batteries consisting of 20 to 100 adjacent ovens with integral flues. Coke oven heating systems fall into two general classes, underjet and gun-flue. In the underjet heating system, the flue gas is introduced into each flue from piping in the basement of the battery. The gas flow to each flue can be metered and controlled. The gun-flue heating system introduces the gas through a horizontal gas duct extending the length of each wall slightly below the floorline of each oven. Short ducts lead upward to a nozzle brick at the bottom of each of the vertical flues in an oven (U.S. EPA, 1987).

Heat for the coking operation is provided by a regenerative combustion system located below the ovens. Because the combustion flue gas contains a significant amount of process heat, two heat regenerators are used for recovery. These regenerators are located below each oven, one for combustion air and one for the combustion waste gas. The flow is alternated between the two at about 30 minute intervals. Hence, coke ovens can be likened to chemical retorts in that they are both batch-operated, fitted with exhaust flues (standpipes), and function without the addition of any reagent.

After the ovens are filled, coking proceeds for 15 to 18 hours to produce “furnace”coke used to convert iron ore to iron in blast furnaces. More time, 25 to 30 hours, is required to produce “foundry” coke, a higher quality type of coke (i.e., higher carbon-containing) used in metal foundries. The coking time is determined by the coal mixture, moisture content of the coal, rate of underfiring, and the desired properties of the coke. The coking temperatures generally range from 1,650 to 2,000°F (900 to 1,100°C) and are kept on the high side of the range to produce blast furnace coke. Air is prevented from leaking into the ovens by maintaining a positive back pressure of about 0.4 in (10 mm) H_2O. The gases and hydrocarbons that are evolved during thermal distillation are removed through the offtake main and sent to the coke byproduct recovery plant (which is described in Section 4.7.3) (U.S. EPA, 1987).

The operation of each oven in the battery is cyclic, but the batteries usually contain a sufficiently large number of ovens (an average of 60) so that the volume of byproduct gas evolved and fed to the byproduct recovery plant is essentially continuous. The individual ovens are charged and discharged at approximately equal time intervals during the coking cycle.

The resultant constant flow of evolved gases from all the ovens in a battery helps to maintain a balance of pressure in the flues, collecting main, and stack. All of the ovens are fired continuously at a constant rate, irrespective of the coking cycle of a particular oven's stage. If damage to the refractory occurs in inaccessible locations through overheating or expansion of coal, repairs may be extremely difficult. A cooldown takes from 5 to 7 weeks, so a battery shutdown is undertaken only as a last alternative (U.S. EPA, 1987).

From the start of the charging operation, POM can be emitted while the hot oven is being filled with coal. Moist coal contacts the hot oven floor and walls and, as a result, the release of volatile components begins immediately. During coking, as volatiles are being driven from the coal, POM can be emitted from leaking side doors and various leaking topside points such as charging port lids and the offtake system that ducts the offgases to the collecting main(s). The techniques and practices that have been developed to control these emissions are listed in Table 4.7-2 (U.S. EPA, 1987).

Staged charging involves pouring coal into the ovens so that an exit space for the generated gases is constantly maintained. The hoppers delivering the coal are discharged such that emissions are contained in the ovens and collecting mains by steam aspiration. Generally, a maximum of two hoppers are discharging at the same time. In sequential charging, to shorten the charging time, the first hoppers are still discharging when subsequent hoppers begin discharging coal. In sequential charging, as with staged charging, the coke ovens are under aspiration. In the use of wet scrubbers on larry cars, the emissions are contained by hoods or shrouds connected to scrubbers that are lowered over the charging ports.

To control leaks from the side doors, the doors can be sealed before the coking process begins. Some doors are designed with a flexible metal band or rigid knife edge as a seal. The seal is formed by condensation of escaping tars on the metal edge of the door. Doors can also be sealed by hand by troweling a mixture called "luting"(a slurry mixture of clay, coal, and other materials) into the opening between the coke oven door and door frame. Luting mixtures are generally prepared by plant personnel according to formulas developed by each plant. The consistency (thickness) of the mixture is adjusted to suit different applications.

TABLE 4.7-2. TECHNIQUES TO CONTROL POM EMISSIONS FROM EMISSION POINTS AT BYPRODUCT COKE PLANTS

Emission Point	Control Technique
Charging Operation	Stage Charging
	Sequential Charging
	Scrubber Systems Mounted on Larry Cars
Door Leaks	Oven Door Seal Technology
	Pressure Differential Devices
	Hoods and Sheds Over Doors
	Operating and Maintenance Procedures
Topside Leaks (Charging Port Lids and Standpipes)	Operating and Maintenance Procedures
Pushing	Hooded, Mobile Scrubber Cars
	Hoods and Sheds Over Doors
	Traveling Hoods Connected to Fixed Control Device
Quenching	Baffles in Quench Tower
	Use of Clean Quench Water Only
	Dry Quenching
Battery Stacks	Operating and Maintenance Procedures
	Containment and Control Devices

Source: Kelly, 1983.

Small cracks and defects in either type of seal can allow pollutants to escape from the coke oven early in the cycle. The magnitude of the leak is determined by the size of the opening, the pressure drop between the oven and the atmosphere, and the composition of the emissions. A pressure differential control device can be used to reduce or reverse the pressure differential across any defects in the door seal. These systems either provide a channel to permit gases that evolve at the bottom of the oven to escape to the collecting main, or the systems provide external pressure on the seal through the use of steam or inert gases.

Oven door emissions also can be reduced by collecting the leaking gases and particulates, and subsequently removing these pollutants from the air stream. A suction hood or shed above each door with a wet electrostatic precipitator for fume removal is an example of this type of system.

Emission control levels for coke oven charging, door leaks, lid leaks, and offtake leaks are categorized as uncontrolled, pre-NESHAP controls, and post-NESHAP controls. Uncontrolled pertains to the control level that characterized coke ovens up to the 1980's; pre-NESHAP controls pertain to the level of control prior to the effective data of the National Emission Standard for Hazardous Air Pollutants (NESHAP) for coke ovens (40 CFR Part 63, Subpart L); and post-NESHAP controls refer to the level of control required by the NESHAP. Table 4.7-3 summarizes these control levels (U.S. EPA, 1995).

Other control techniques rely on operating and maintenance procedures rather than only hardware. Operating procedures for emission reduction could include changes in the oven cycle times and temperatures; the amount and placement of each charge; and any adjustments of the end-door while the oven is on line. Maintenance procedures include routine inspection, replacement, and repair of control devices and doors.

Topside leaks occurring from rims of charging ports and standpipe leaks on the top of the coke oven can be controlled primarily by proper maintenance and operating procedures that include:

- Replacement of warped lids;

TABLE 4.7-3. EMISSION CONTROL LEVELS FOR CHARGING AND DOOR, LID, AND OFFTAKE LEAKS[a]

Source	Uncontrolled	Pre-NESHAP Controls	Post-NESHAP Controls
Charging (SCC-3-03-003-02)	3 to 5 minutes/charge	Stage charging, 25 to 30 seconds/charge, 44 g BSO/charge	Stage charging, steam aspiration, 10 seconds/charge, 5 g BSO/charge
Door Leaks (SCC 3-03-003-08)	29 to 70 percent leaking (average 50 percent)	10 percent leaking	4 percent leaking
Lid Leaks (SCC 3-03-003-14)	25 percent leaking	3.5 percent leaking	0.3 percent leaking
Offtake Leaks (SCC 3-03-003-14)	50 percent leaking	6.5 percent leaking	2.0 percent leaking

[a] SCC=Source Classification Code.

- Cleaning carbon deposits or other obstructions from the mating surfaces of lids or their seats;
- Patching or replacing cracked standpipes;
- Sealing lids with lute after a charge or whenever necessary; and
- Sealing cracks at the base of a standpipe with lute.

Emission Factors

Limited emission factor data exist for individual POM species emissions from the different operations in the byproduct coking process. The quantity and composition of emissions from coking processes are highly variable because coking conditions can vary widely from plant to plant and within the same plant from process to process. Coal composition and moisture content vary widely, and these process variables can have a significant bearing on emissions. Coking times and temperatures can also be varied so as to have marked impacts on potential POM emissions. The fugitive nature of the majority of coking process emissions complicates emissions control and increases the potential for widely varying emission estimates.

Emission factors for BSO from different points in coke ovens are listed in Table 4.7-4. The emission factors for charging, door leaks, lid leaks, and offtake leaks are listed for each of the control scenaries (uncontrolled, pre-NESHAP, post-NESHAP) summarized previously in Table 4.7-3. With the exeception of the factors for uncontrolled charging and uncontrolled door leaks, the emission factors for leaks and charging given in Table 4.7-4 are based on an average or typical battery. These emission factors may be useful if site-specific information (other than capacity) is not available for the battery. The preferred approach for a specific battery is to use the actual number of emission points on the battery and historical data for control of visible emissions, such as the annual average percent of the doors that leak.

The distribution of BSO emissions from the charging, door, and topside leaks as a percentage of emissions from all coke oven emissions prior to the passage of the 1993 MACT standard was estimated to be as follows:

TABLE 4.7-4. BSO EMISSION FACTORS FOR COKE OVEN SOURCES[a]

Source	BSO[b]	
	kg/Mg	lb/ton
Charging[c]		
(SCC 3-03-003-02)		
Uncontrolled	0.44	0.88
Pre-NESHAP controls	0.0027	0.0053
Post-NESHAP controls	0.00030	0.00060
Door Leaks[c,d]		
(SCC-3-03-003-08)		
Uncontrolled	0.28	0.55
Pre-NESHAP controls	0.011	0.022
Post-NESHAP controls	0.0044	0.0088
Lid Leaks[c,d]		
(SCC 3-03-003-14)		
Uncontrolled	0.025	0.050
Pre-NESHAP controls	0.0036	0.0071
Post-NESHAP controls	0.00030	0.00060
Offtake leaks[c,d]		
(SCC 3-03-003-14)		
Uncontrolled	0.025	0.050
Pre-NESHAP controls	0.0033	0.0066
Post-NESHAP controls	0.0010	0.0020
Coke Pushing[e]		
(SCC 3-03-003-03)	0.008-0.017	0.016-0.034
Coke Quenching[e]		
(SCC 3-03-003-04)	0.011-2.8	0.022-5.6
Battery Stacks[e]		
(SCC 3-03-003-17)	0.0016	0.0032

[a] Emission factors in lb/ton (kg/Mg) of coal charged. SCC = Source Classification Code.
[b] BSO = benzene soluble organics.
[c] Source: U.S. EPA, 1995.
[d] For site-specific estimates based on the average number of leaks, estimate BSO as follows:
Average number of doors leaking x 0.05 = door leak emission rate, kg/hr;
Average number of lids leaking x 0.023 = lid leak emission rate, kg/hr; and
Average number of offtakes leaking x 0.023 = offtake leak emission rate, kg/hr.
[e] Source: Trenholm and Beck, 1978.

- About 5 percent from oven charging;
- About 81 percent from coke oven door leaks; and
- About 14 percent from topside point leaks.

These percentages reflect both the amount of total coke oven emissions expected from each type of point and the BSO content of the emissions from each type of point. For instance, there is a lower quantity of BSO (and hence POM) in charging emissions than in those from leaks, and more coke oven emissions in general are associated with door leaks than the other two points (57 FR 57534).

Similarly, benzo(a)pyrene has also been measured as a surrogate for total POM. Reported measurements of benzo(a)pyrene from the three different emission points also vary by orders of magnitude for different emission tests. The variability in measurements is again due to the time into the coking cycle and temperature when sampling occurred, type of coal, analytical techniques, or other differences between batteries. However, tests find the level of benzo(a)pyrene in coke oven emissions overall is generally 1 percent of measured BSO (U.S. EPA, 1987).

Emission factors for POM from charging, door, and topside leaks are given in Table 4.7-5. The emission factors for individual PAHs including benzo(a)pyrene were derived from the BSO emission factors reported in Table 4.7-4. Only a few researchers have attempted to quantify the individual components in coke oven gas, and no attempt to speciate BSO contained in coke oven gas could be found. A thorough analysis of organic matter in coke oven emissions was reported by Kirton et al., 1991. The analysis included all organics containing six and more carbons and their percentage contribution to the total organic content.

Using the information that BSO represents roughly the organic compounds containing 16 or more carbons and benzo(a)pyrene represents one percent of BSO in general, the speciation profile of BSO shown in Table 4.7-1 was developed from the Kirton et al. report. Individual PAH emission factors were calculated by multiplying the BSO emission factors

TABLE 4.7-5. POM EMISSION FACTORS FOR COKE OVENS: CHARGING, DOOR, LID AND OFFTAKE LEAKS

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-02	Oven Charging-	Uncontrolled	Benz(a)anthracene	1.68E-02 (8.40E-03)	E
			Benzo(a)pyrene	1.21E-02 (6.07E-03)	E
			Benzo(b)fluoranthene	1.50E-02 (7.52E-03)	E
			Benzo(j+k)fluoranthene	1.07E-02 (5.37E-03)	E
			Chrysene/ Triphenylene	1.80E-02 (8.98E-03)	E
			Dibenz(a,h)anthracene	1.41E-03 (7.04E-04)	E
			Indeno(1,2,3-cd)pyrene	5.72E-03 (2.86E-03)	E
			Acenaphthene	1.04E-02 (5.19E-03)	E
			Acenaphthylene	5.02E-02 (2.51E-02)	E
			Anthracene	3.01E-02 (1.50E-02)	E
			Benzo(ghi)perylene	5.37E-03 (2.68E-03)	E
			Fluoranthene	5.48E-02 (2.74E-02)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-02 (continued)	Oven Charging (continued)	Uncontrolled (continued)	Fluorene	3.44E-02 (1.72E-02)	E
			Naphthalene	1.76E-01 (8.80E-02)	E
			Phenanthrene	1.20E-01 (5.98E-02)	E
			Pyrene	3.77E-02 (1.88E-02)	E
			1-Methylnaphthalene	2.73E-02 (1.36E-02)	E
			2-Methylnaphthalene	5.95E-02 (2.97E-02)	E
			Benzo(e)pyrene	1.14E-02 (5.72E-03)	E
			Biphenyl	1.33E-02 (6.64E-03)	E
			Di- and Trimethylnaphthalenes	5.81E-02 (2.90E-02)	E
			Dibenzofuran	4.66E-02 (2.33E-02)	E
			Methyl- and Dimethyldibenzofurans	1.80E-02 (8.98E-03)	E
			Methylacenaphthylenes	1.04E-02 (5.19E-03)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-02 (continued)	Oven Charging (continued)	Uncontrolled (continued)	Methylbenzfluoranthenes/ Methylbenzpyrene	2.01E-02 (1.00E-02)	E
			Methylbiphenyls	1.07E-02 (5.37E-03)	E
			Methylfluorenes	2.47E-02 (1.24E-02)	E
			Methylphenanthrenes/ Methylanthracenes	2.01E-02 (1.00E-02)	E
3-03-003-02	Oven Charging	Pre-NESHAP Controls	Benz(a)anthracene	1.01E-04 (5.16E-05)	E
			Benzo(a)pyrene	7.31E-05 (3.73E-05)	E
			Benzo(b)fluoranthene	9.06E-05 (4.62E-05)	E
			Benzo(j+k)fluoranthene	6.47E-05 (3.29E-05)	E
			Chrysene/ Triphenylene	1.08E-04 (5.51E-05)	E
			Dibenz(a,h)anthracene	8.48E-06 (4.32E-06)	E
			Indeno(1,2,3-cd)pyrene	3.45E-05 (1.76E-05)	E
			Acenaphthene	6.25E-05 (3.19E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-02 (continued)	Oven Charging (continued)	Pre-NESHAP Controls (continued)	Acenaphthylene	3.02E-04 (1.54E-04)	E
			Anthracene	1.81E-04 (9.23E-05)	E
			Benzo(ghi)perylene	3.23E-05 (1.65E-05)	E
			Fluoranthene	3.30E-04 (1.68E-04)	E
			Fluorene	2.07E-04 (1.06E-04)	E
			Naphthalene	1.06E-03 (5.40E-04)	E
			Phenanthrene	7.21E-04 (3.67E-04)	E
			Pyrene	2.27E-04 (1.16E-04)	E
			1-Methylnaphthalene	1.64E-04 (8.37E-05)	E
			2-Methylnaphthalene	3.58E-04 (1.83E-04)	E
			Benzo(e)pyrene	6.89E-05 (3.51E-05)	E
			Biphenyl	8.00E-05 (4.08E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-02 (continued)	Oven Charging (continued)	Pre-NESHAP Controls (continued)	Di- and Trimethylnaphthalenes	3.50E-04 (1.78E-04)	E
			Dibenzofuran	2.81E-04 (1.43E-04)	E
			Methyl- and Dimethyldibenzofurans	1.08E-04 (5.51E-05)	E
			Methylacenaphthylenes	6.25E-05 (3.19E-05)	E
			Methylbenzfluoranthenes/ Methylbenzpyrenes	1.21E-04 (6.16E-05)	E
			Methylbiphenyls	6.47E-05 (3.29E-05)	E
			Methylfluorenes	1.49E-04 (7.59E-05)	E
			Methylphenanthrenes/ Methylanthracenes	1.21E-04 (6.16E-05)	E
3-03-003-02	Oven Charging	Post-NESHAP Controls	Benz(a)anthracene	1.15E-05 (5.73E-06)	E
			Benzo(a)pyrene	8.28E-06 (4.14E-06)	E
			Benzo(b)fluoranthene	1.03E-05 (5.13E-06)	E
			Benzo(j+k)fluoranthene	7.32E-06 (3.66E-06)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-02 (continued)	Oven Charging (continued)	Post-NESHAP Controls (continued)	Chrysene/ Triphenylene	1.22E-05 (6.12E-06)	E
			Dibenz(a,h)anthracene	9.60E-07 (4.80E-07)	E
			Indeno(1,2,3-cd)pyrene	3.90E-06 (1.95E-06)	E
			Acenaphthene	7.08E-06 (3.54E-06)	E
			Acenaphthylene	3.42E-05 (1.71E-05)	E
			Anthracene	2.05E-05 (1.03E-05)	E
			Benzo(ghi)perylene	3.66E-06 (1.83E-06)	E
			Fluoranthene	3.74E-05 (1.87E-05)	E
			Fluorene	2.35E-05 (1.17E-05)	E
			Naphthalene	1.20E-04 (6.00E-05)	E
			Phenanthrene	8.16E-05 (4.08E-05)	E
			Pyrene	2.57E-05 (1.28E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-02 (continued)	Oven Charging (continued)	Post-NESHAP Controls (continued)	1-Methylnaphthalene	1.86E-05 (9.30E-06)	E
			2-Methylnaphthalene	4.06E-05 (2.03E-05)	E
			Benzo(e)pyrene	7.80E-06 (3.90E-06)	E
			Biphenyl	9.06E-06 (4.53E-06)	E
			Di- and Trimethylnaphthalenes	3.96E-05 (1.98E-05)	E
			Dibenzofuran	3.18E-05 (1.59E-05)	E
			Methyl- and Dimethyldibenzofurans	1.22E-05 (6.12E-06)	E
			Methylacenaphthylenes	7.08E-06 (3.54E-06)	E
			Methylbenzfluoranthenes/ Methylbenzpyrene	1.37E-05 (6.84E-06)	E
			Methylbiphenyls	7.32E-06 (3.66E-06)	E
			Methylfluorenes	1.69E-05 (8.43E-06)	E
			Methylphenanthrenes/ Methylanthracenes	1.37E-05 (6.84E-06)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-08	Door Leaks	Uncontrolled	Benz(a)anthracene	1.05E-02 (5.35E-03)	E
			Benzo(a)pyrene	7.59E-03 (3.86E-03)	E
			Benzo(b)fluoranthene	9.41E-03 (4.79E-03)	E
			Benzo(j+k)fluoranthene	6.71E-03 (3.42E-03)	E
			Chrysene/ Triphenylene	1.12E-02 (5.71E-03)	E
			Dibenz(a,h)anthracene	8.80E-04 (4.48E-04)	E
			Indeno(1,2,3-cd)pyrene	3.58E-03 (1.82E-03)	E
			Acenaphthene	6.49E-03 (3.30E-03)	E
			Acenaphthylene	3.14E-02 (1.60E-02)	E
			Anthracene	1.88E-02 (9.58E-03)	E
			Benzo(ghi)perylene	3.36E-03 (1.71E-03)	E
			Fluoranthene	3.43E-02 (1.74E-02)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-08 (continued)	Door Leaks (continued)	Uncontrolled (continued)	Fluorene	2.15E-02 (1.09E-02)	E
			Naphthalene	1.10E-01 (5.60E-02)	E
			Phenanthrene	7.48E-02 (3.81E-02)	E
			Pyrene	2.35E-02 (1.20E-02)	E
			1-Methylnaphthalene	1.71E-02 (8.68E-03)	E
			2-Methylnaphthalene	3.72E-02 (1.89E-02)	E
			Benzo(e)pyrene	7.15E-03 (3.64E-03)	E
			Biphenyl	8.31E-03 (4.23E-03)	E
			Di- and Trimethylnaphthalenes	3.63E-02 (1.85E-02)	E
			Dibenzofuran	2.92E-02 (1.48E-02)	E
			Methyl- and Dimethyldibenzofurans	1.12E-02 (5.71E-03)	E
			Methylacenaphthylenes	6.49E-03 (3.30E-03)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-08 (continued)	Door Leaks (continued)	Uncontrolled (continued)	Methylbenzfluoranthenes/ Methylbenzpyrenes	1.25E-02 (6.38E-03)	E
			Methylbiphenyls	6.71E-03 (3.42E-03)	E
			Methylfluorenes	1.55E-02 (7.87E-03)	E
			Methylphenanthrenes/ Methylanthracenes	1.25E-02 (6.38E-03)	E
3-03-003-08	Door Leaks	Pre-NESHAP Controls	Benz(a)anthracene	4.20E-04 (2.10E-04)	E
			Benzo(a)pyrene	3.04E-04 (1.52E-04)	E
			Benzo(b)fluoranthene	3.76E-04 (1.88E-04)	E
			Benzo(j+k)fluoranthene	2.68E-04 (1.34E-04)	E
			Chrysene/ Triphenylene	4.49E-04 (2.24E-04)	E
			Dibenz(a,h)anthracene	3.52E-05 (1.76E-05)	E
			Indeno(1,2,3-cd)pyrene	1.43E-04 (7.15E-05)	E
			Acenaphthene	2.60E-04 (1.30E-04)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-08 (continued)	Door Leaks (continued)	Pre-NESHAP Controls (continued)	Acenaphthylene	1.25E-03 (6.27E-04)	E
			Anthracene	7.52E-04 (3.76E-04)	E
			Benzo(ghi)perylene	1.34E-04 (6.71E-05)	E
			Fluoranthene	1.37E-03 (6.85E-04)	E
			Fluorene	8.60E-04 (4.30E-04)	E
			Naphthalene	4.40E-03 (2.20E-03)	E
			Phenanthrene	2.99E-03 (1.50E-03)	E
			Pyrene	9.42E-04 (4.71E-04)	E
			1-Methylnaphthalene	6.82E-04 (3.41E-04)	E
			2-Methylnaphthalene	1.49E-03 (7.44E-04)	E
			Benzo(e)pyrene	2.86E-04 (1.43E-04)	E
			Biphenyl	3.32E-04 (1.66E-04)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-08 (continued)	Door Leaks (continued)	Pre-NESHAP Controls (continued)	Di- and Trimethylnaphthalenes	1.45E-03 (7.26E-04)	E
			Dibenzofuran	1.17E-03 (5.83E-04)	E
			Methyl- and Dimethyldibenzofurans	4.49E-04 (2.24E-04)	E
			Methylacenaphthylenes	2.60E-04 (1.30E-04)	E
			Methylbenzfluoranthenes/ Methylbenzpyrene	5.02E-04 (2.51E-04)	E
			Methylbiphenyls	2.68E-04 (1.34E-04)	E
			Methylfluorenes	6.18E-04 (3.09E-04)	E
			Methylphenanthrenes/ Methylanthracenes	5.02E-04 (2.51E-04)	E
3-03-003-08	Door Leaks	Post-NESHAP Controls	Benz(a)anthracene	1.68E-04 (8.40E-05)	E
			Benzo(a)pyrene	1.21E-04 (6.07E-05)	E
			Benzo(b)fluoranthene	1.50E-04 (7.52E-05)	E
			Benzo(j+k)fluoranthene	1.07E-04 (5.37E-05)	E

(continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-08 (continued)	Door Leaks (continued)	Post-NESHAP Controls (continued)	Chrysene/ Triphenylene	1.80E-04 (8.98E-05)	E
			Dibenz(a,h)anthracene	1.41E-05 (7.04E-06)	E
			Indeno(1,2,3-cd)pyrene	5.72E-05 (2.86E-05)	E
			Acenaphthene	1.04E-04 (5.19E-05)	E
			Acenaphthylene	5.02E-04 (2.51E-04)	E
			Anthracene	3.01E-04 (1.50E-04)	E
			Benzo(ghi)perylene	5.37E-05 (2.68E-05)	E
			Fluoranthene	5.48E-04 (2.74E-04)	E
			Fluorene	3.44E-04 (1.72E-04)	E
			Naphthalene	1.76E-03 (8.80E-04)	E
			Phenanthrene	1.20E-03 (5.98E-04)	E
			Pyrene	3.77E-04 (1.88E-04)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-08 (continued)	Door Leaks (continued)	Post-NESHAP Controls (continued)	1-Methylnaphthalene	2.73E-04 (1.36E-04)	E
			2-Methylnaphthalene	5.95E-04 (2.97E-04)	E
			Benzo(e)pyrene	1.14E-04 (5.72E-05)	E
			Biphenyl	1.33E-04 (6.64E-05)	E
			Di- and Trimethylnaphthalenes	5.81E-04 (2.90E-04)	E
			Dibenzofuran	4.66E-04 (2.33E-04)	E
			Methyl- and Dimethyldibenzofurans	1.80E-04 (8.98E-05)	E
			Methylacenaphthylenes	1.04E-04 (5.19E-05)	E
			Methylbenzfluoranthenes/ Methylbenzpyrenes	2.01E-04 (1.00E-04)	E
			Methylbiphenyls	1.07E-04 (5.37E-05)	E
			Methylfluorenes	2.47E-04 (1.24E-04)	E
			Methylphenanthrenes/ Methylanthracenes	2.01E-04 (1.00E-04)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14	Lid Leaks	Uncontrolled	Benz(a)anthracene	9.55E-04 (4.78E-04)	E
			Benzo(a)pyrene	6.90E-04 (3.45E-04)	E
			Benzo(b)fluoranthene	8.55E-04 (4.28E-04)	E
			Benzo(j+k)fluoranthene	6.10E-04 (3.05E-04)	E
			Chrysene/ Triphenylene	1.02E-03 (5.10E-04)	E
			Dibenz(a,h)anthracene	8.00E-05 (4.00E-05)	E
			Indeno(1,2,3-cd)pyrene	3.25E-04 (1.63E-04)	E
			Acenaphthene	5.90E-04 (2.95E-04)	E
			Acenaphthylene	2.85E-03 (1.43E-03)	E
			Anthracene	1.71E-03 (8.55E-04)	E
			Benzo(ghi)perylene	3.05E-04 (1.53E-04)	E
			Fluoranthene	3.12E-03 (1.56E-03)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Lid Leaks (continued)	Uncontrolled (continued)	Fluorene	1.96E-03 (9.78E-04)	E
			Naphthalene	1.00E-02 (5.00E-03)	E
			Phenanthrene	6.80E-03 (3.40E-03)	E
			Pyrene	2.14E-03 (1.07E-03)	E
			1-Methylnaphthalene	1.55E-03 (7.75E-04)	E
			2-Methylnaphthalene	3.38E-03 (1.69E-03)	E
			Benzo(e)pyrene	6.50E-04 (3.25E-04)	E
			Biphenyl	7.55E-04 (3.78E-04)	E
			Di- and Trimethylnaphthalenes	3.30E-03 (1.65E-03)	E
			Dibenzofuran	2.65E-03 (1.33E-03)	E
			Methyl- and Dimethyldibenzofurans	1.02E-03 (5.10E-04)	E
			Methylacenaphthylenes	5.90E-04 (2.95E-04)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Lid Leaks (continued)	Uncontrolled (continued)	Methylbenzfluoranthenes/ Methylbenzpyrenes	1.14E-03 (5.70E-04)	E
			Methylbiphenyls	6.10E-04 (3.05E-04)	E
			Methylfluorenes	1.41E-03 (7.03E-04)	E
			Methylphenanthrenes/ Methylanthracenes	1.14E-03 (5.70E-04)	E
3-03-003-14	Lid Leaks	Pre-NESHAP Controls	Benz(a)anthracene	1.36E-04 (6.88E-05)	E
			Benzo(a)pyrene	9.80E-05 (4.97E-05)	E
			Benzo(b)fluoranthene	1.21E-04 (6.16E-05)	E
			Benzo(j+k)fluoranthene	8.66E-05 (4.39E-05)	E
			Chrysene/ Triphenylene	1.45E-04 (7.34E-05)	E
			Dibenz(a,h)anthracene	1.14E-05 (5.76E-06)	E
			Indeno(1,2,3-cd)pyrene	4.62E-05 (2.34E-05)	E
			Acenaphthene	8.38E-05 (4.25E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Lid Leaks (continued)	Pre-NESHAP Controls (continued)	Acenaphthylene	4.05E-04 (2.05E-04)	E
			Anthracene	2.43E-04 (1.23E-04)	E
			Benzo(ghi)perylene	4.33E-05 (2.20E-05)	E
			Fluoranthene	4.42E-04 (2.24E-04)	E
			Fluorene	2.78E-04 (1.41E-04)	E
			Naphthalene	1.42E-03 (7.20E-04)	E
			Phenanthrene	9.66E-04 (4.90E-04)	E
			Pyrene	3.04E-04 (1.54E-04)	E
			1-Methylnaphthalene	2.20E-04 (1.12E-04)	E
			2-Methylnaphthalene	4.80E-04 (2.43E-04)	E
			Benzo(e)pyrene	9.23E-05 (4.68E-05)	E
			Biphenyl	1.07E-04 (5.44E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Lid Leaks (continued)	Pre-NESHAP Controls (continued)	Di- and Trimethylnaphthalenes	4.69E-04 (2.38E-04)	E
			Dibenzofuran	3.76E-04 (1.91E-04)	E
			Methyl- and Dimethyldibenzofurans	1.45E-04 (7.34E-05)	E
			Methylacenaphthylenes	8.38E-05 (4.25E-05)	E
			Methylbenzfluoranthenes/ Methylbenzpyrenes	1.62E-04 (8.21E-05)	E
			Methylbiphenyls	8.66E-05 (4.39E-05)	E
			Methylfluorenes	2.00E-04 (1.01E-04)	E
			Methylphenanthrenes/ Methylanthracenes	1.62E-04 (8.21E-05)	E
3-03-003-14	Lid Leaks	Post-NESHAP Controls	Benz(a)anthracene	1.15E-05 (5.73E-06)	E
			Benzo(a)pyrene	8.28E-06 (4.14E-06)	E
			Benzo(b)fluoranthene	1.03E-05 (5.13E-06)	E
			Benzo(j+k)fluoranthene	7.32E-06 (3.66E-06)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Lid Leaks (continued)	Post-NESHAP Controls (continued)	Chrysene/ Triphenylene	1.22E-05 (6.12E-06)	E
			Dibenz(a,h)anthracene	9.60E-07 (4.80E-07)	E
			Indeno(1,2,3-cd)pyrene	3.90E-06 (1.95E-06)	E
			Acenaphthene	7.08E-06 (3.54E-06)	E
			Acenaphthylene	3.42E-05 (1.71E-05)	E
			Anthracene	2.05E-05 (1.03E-05)	E
			Benzo(ghi)perylene	3.66E-06 (1.83E-06)	E
			Fluoranthene	3.74E-05 (1.87E-05)	E
			Fluorene	2.35E-05 (1.17E-05)	E
			Naphthalene	1.20E-04 (6.00E-05)	E
			Phenanthrene	8.16E-05 (4.08E-05)	E
			Pyrene	2.57E-05 (1.28E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Lid Leaks (continued)	Post-NESHAP Controls (continued)	1-Methylnaphthalene	1.86E-05 (9.30E-06)	E
			2-Methylnaphthalene	4.06E-05 (2.03E-05)	E
			Benzo(e)pyrene	7.80E-06 (3.90E-06)	E
			Biphenyl	9.06E-06 (4.53E-06)	E
			Di- and Trimethylnaphthalenes	3.96E-05 (1.98E-05)	E
			Dibenzofuran	3.18E-05 (1.59E-05)	E
			Methyl- and Dimethyldibenzofurans	1.22E-05 (6.12E-06)	E
			Methylacenaphthylenes	7.08E-06 (3.54E-06)	E
			Methylbenzfluoranthenes/ Methylbenzpyrenes	1.37E-05 (6.84E-06)	E
			Methylbiphenyls	7.32E-06 (3.66E-06)	E
			Methylfluorenes	1.69E-05 (8.43E-06)	E
			Methylphenanthrenes/ Methylanthracenes	1.37E-05 (6.84E-06)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14	Offtake Leaks	Uncontrolled	Benz(a)anthracene	9.55E-04 (4.78E-04)	E
			Benzo(a)pyrene	6.90E-04 (3.45E-04)	E
			Benzo(b)fluoranthene	8.55E-04 (4.28E-04)	E
			Benzo(j+k)fluoranthene	6.10E-04 (3.05E-04)	E
			Chrysene/ Triphenylene	1.02E-03 (5.10E-04)	E
			Dibenz(a,h)anthracene	8.00E-05 (4.00E-05)	E
			Indeno(1,2,3-cd)pyrene	3.25E-04 (1.63E-04)	E
			Acenaphthene	5.90E-04 (2.95E-04)	E
			Acenaphthylene	2.85E-03 (1.43E-03)	E
			Anthracene	1.71E-03 (8.55E-04)	E
			Benzo(ghi)perylene	3.05E-04 (1.53E-04)	E
			Fluoranthene	3.12E-03 (1.56E-03)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Offtake Leaks (continued)	Uncontrolled (continued)	Fluorene	1.96E-03 (9.78E-04)	E
			Naphthalene	1.00E-02 (5.00E-03)	E
			Phenanthrene	6.80E-03 (3.40E-03)	E
			Pyrene	2.14E-03 (1.07E-03)	E
			1-Methylnaphthalene	1.55E-03 (7.75E-04)	E
			2-Methylnaphthalene	3.38E-03 (1.69E-03)	E
			Benzo(e)pyrene	6.50E-04 (3.25E-04)	E
			Biphenyl	7.55E-04 (3.78E-04)	E
			Di- and Trimethylnaphthalenes	3.30E-03 (1.65E-03)	E
			Dibenzofuran	2.65E-03 (1.33E-03)	E
			Methyl- and Dimethyldibenzofurans	1.02E-03 (5.10E-04)	E
			Methylacenaphthylenes	5.90E-04 (2.95E-04)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Offtake Leaks (continued)	Uncontrolled (continued)	Methylbenzfluoranthenes/ Methylbenzpyrenes	1.14E-03 (5.70E-04)	E
			Methylbiphenyls	6.10E-04 (3.05E-04)	E
			Methylfluorenes	1.41E-03 (7.03E-04)	E
			Methylphenanthrenes/ Methylanthracenes	1.14E-03 (5.70E-04)	E
3-03-003-14	Offtake Leaks	Pre-NESHAP Controls	Benz(a)anthracene	1.26E-04 (6.30E-05)	E
			Benzo(a)pyrene	9.11E-05 (4.55E-05)	E
			Benzo(b)fluoranthene	1.13E-04 (5.64E-05)	E
			Benzo(j+k)fluoranthene	8.05E-05 (4.03E-05)	E
			Chrysene/ Triphenylene	1.35E-04 (6.73E-05)	E
			Dibenz(a,h)anthracene	1.06E-05 (5.28E-06)	E
			Indeno(1,2,3-cd)pyrene	4.29E-05 (2.15E-05)	E
			Acenaphthene	7.79E-05 (3.89E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Offtake Leaks (continued)	Pre-NESHAP Controls (continued)	Acenaphthylene	3.76E-04 (1.88E-04)	E
			Anthracene	2.26E-04 (1.13E-04)	E
			Benzo(ghi)perylene	4.03E-05 (2.01E-05)	E
			Fluoranthene	4.11E-04 (2.06E-04)	E
			Fluorene	2.58E-04 (1.29E-04)	E
			Naphthalene	1.32E-03 (6.60E-04)	E
			Phenanthrene	8.98E-04 (4.49E-04)	E
			Pyrene	2.82E-04 (1.41E-04)	E
			1-Methylnaphthalene	2.05E-04 (1.02E-04)	E
			2-Methylnaphthalene	4.46E-04 (2.23E-04)	E
			Benzo(e)pyrene	8.58E-05 (4.29E-05)	E
			Biphenyl	9.97E-05 (4.98E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Offtake Leaks (continued)	Pre-NESHAP Controls (continued)	Di- and Trimethylnaphthalenes	4.36E-04 (2.18E-04)	E
			Dibenzofuran	3.50E-04 (1.75E-04)	E
			Methyl- and Dimethyldibenzofurans	1.35E-04 (6.73E-05)	E
			Methylacenaphthylenes	7.79E-05 (3.89E-05)	E
			Methylbenzfluoranthenes/ Methylbenzpyrenes	1.50E-04 (7.52E-05)	E
			Methylbiphenyls	8.05E-05 (4.03E-05)	E
			Methylfluorenes	1.85E-04 (9.27E-05)	E
			Methylphenanthrenes/ Methylanthracenes	1.50E-04 (7.52E-05)	E
3-03-003-14	Offtake Leaks	Post-NESHAP Controls	Benz(a)anthracene	3.82E-05 (1.91E-05)	E
			Benzo(a)pyrene	2.76E-05 (1.38E-05)	E
			Benzo(b)fluoranthene	3.42E-05 (1.71E-05)	E
			Benzo(j+k)fluoranthene	2.44E-05 (1.22E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Offtake Leaks (continued)	Post-NESHAP Controls (continued)	Chrysene/ Triphenylene	4.08E-05 (2.04E-05)	E
			Dibenz(a,h)anthracene	3.20E-06 (1.60E-06)	E
			Indeno(1,2,3-cd)pyrene	1.30E-05 (6.50E-06)	E
			Acenaphthene	2.36E-05 (1.18E-05)	E
			Acenaphthylene	1.14E-04 (5.70E-05)	E
			Anthracene	6.84E-05 (3.42E-05)	E
			Benzo(ghi)perylene	1.22E-05 (6.10E-06)	E
			Fluoranthene	1.25E-04 (6.23E-05)	E
			Fluorene	7.82E-05 (3.91E-05)	E
			Naphthalene	4.00E-04 (2.00E-04)	E
			Phenanthrene	2.72E-04 (1.36E-04)	E
			Pyrene	8.56E-05 (4.28E-05)	E

(continued)

TABLE 4.7-5. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-14 (continued)	Offtake Leaks (continued)	Post-NESHAP Controls (continued)	1-Methylnaphthalene	6.20E-05 (3.10E-05)	E
			2-Methylnaphthalene	1.35E-04 (6.76E-05)	E
			Benzo(e)pyrene	2.60E-05 (1.30E-05)	E
			Biphenyl	3.02E-05 (1.51E-05)	E
			Di- and Trimethylnaphthalenes	1.32E-04 (6.60E-05)	E
			Dibenzofuran	1.06E-04 (5.30E-05)	E
			Methyl- and Dimethyldibenzofurans	4.08E-05 (2.04E-05)	E
			Methylacenaphthylenes	2.36E-05 (1.18E-05)	E
			Methylbenzfluoranthenes/ Methylbenzpyrenes	4.56E-05 (2.28E-05)	E
			Methylbiphenyls	2.44E-05 (1.22E-05)	E
			Methylfluorenes	5.62E-05 (2.81E-05)	E
			Methylphenanthrenes/ Methylanthracenes	4.56E-05 (2.28E-05)	E

[a] Emission factors in lb/ton (kg/Mg) of coal charged.

(continued)

listed in Table 4.7-4 by the percentage of a particular PAH or POM found in BSO listed in Table 4.7-1. Emission factors were calculated for all the 16 priority PAH and for those POM compounds that individually constitute greater than 1 percent of BSO. The 1 percent cut-off was used in order to allow for a more manageable presentation of the factors in Table 4.7-5; factors developed for POM compounds below the 1 percent cut-off result in a very small quantity of emissions relative to the overall source categories. It must be reemphasized that these are order-of-magnitude estimates mainly due to the variability in the composition of coke oven gas.

The uncontrolled emission factors reported are for poorly controlled batteries. With the exception of charging, an uncontrolled condition is difficult to define for the various coke oven emission points because routine operations involve some degree of control. Any emission estimate for a specific battery should consider the number of leaking doors, lids, or offtakes and the range of emission rates from these points (U.S. EPA, 1987).

Hence, the 1993 MACT standard governing emissions during charging and from door and topside leaks does not specify the control techniques to be used. Instead, the standard limits visible emissions, which has been the typical regulatory approach used by States and internationally. Coke plant owners and operators can choose from the known control techniques listed in Table 4.7-2 to comply with the visible emissions limitations. It is estimated that when the 1993 MACT standard is fully implemented, nationwide coke oven emissions from charging and leaks will be reduced to 300 tpy (270 Mg/yr) or by about 66 percent by the end of 1995 (57 FR 57534).

Source Locations

In 1983, 25.8 million tons (23.5 million Mg) of coke were produced in U.S. byproduct coke ovens (U.S. EPA, 1987). At the end of 1990, the industry’s total production capacity was estimated to be 30 million tpy (27 million Mg/yr) coke (actual 1990 production being somewhat lower). Table 4.7-6 lists the operating U.S. byproduct coke plants and the identification number of the batteries located at the plant (57 FR 57534).

TABLE 4.7-6. COKE OVEN BATTERIES CURRENTLY OPERATING IN THE UNITED STATES

Plant (Location)	Battery Identification Number
ABC Coke (Tarrant, AL)	A
	5
	6
Acme Steel (Chicago, IL)	1
	2
Armco, Inc. (Middletown, OH)	1
	2
	3
Armco, Inc. (Ashland, KY)	3
	4
Bethlehem Steel (Bethlehem, PA)	A
	2
	3
Bethlehem Steel (Burns Harbor, IN)	1
	2
Bethlehem Steel (Lackawanna, NY)	7
	8
Citizens Gas (Indianapolis, IN)	E
	H
	1
Empire Coke (Holt, AL)	1
	2
Erie Coke (Erie, PA)	A
	B

(continued)

TABLE 4.7-6. (Continued)

Plant (Location)	Battery Identification Number
Geneva Steel (Provo, UT)	1
	2
	3
	4
Gulf States Steel (Gadsden, AL)	2
	3
Inland Steel (East Chicago, IN)	6
	7
	9
	10
	11
Koppers (Woodward, AL)	1
	2A
	2B
	4A
	4B
	5
LTV Steel (Cleveland, OH)	6
	7
LTV Steel (Pittsburgh, PA)	P1
	P2
	P3N
	P3S
	P4
LTV Steel (Chicago, IL)	2
LTV Steel (Warren, OH)	4

(continued)

TABLE 4.7-6. (Continued)

Plant (Location)	Battery Identification Number
National Steel (Ecorse, MI)	5
National Steel (Granite City, IL)	A
	B
New Boston Coke (Portsmouth, OH)	1
Sharon Steel (Monessen, PA)	1B
	2
Shenango (Pittsburgh, PA)	1
	4
Sloss Industries (Birmingham, AL)	3
	4
	5
Toledo Coke (Toledo, OH)	C
Tonawanda Coke (Buffalo, NY)	1
USX (Clairton, PA)	1
	2
	3
	7
	8
	9
	13
	14
	15
	19
	20
	B

(continued)

TABLE 4.7-6. (Continued)

Plant (Location)	Battery Identification Number
USX (Gary, IN)	23
	5
	7
Wheeling-Pittsburgh (East Steubenville, WV)	1
	2
	3
	8

NOTE: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular 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. These operating plants and locations were current as of April 1, 1992.

Source: 57 FR 57534.

4.7.2 Coke Ovens: Pushing, Quenching, and Battery Stacks

Process Description

Although the large majority of coke oven emissions occur during charging and from door and topside leaks during coking, some POM may be emitted from battery exhaust stacks during coking and afterwards during product handling. Because the emissions from battery stacks and product handling are small compared to those from charging, door, and topside leaks, these emissions were not addressed in the 1993 MACT standard. Instead, they will be the focus of an upcoming rulemaking (57 FR 57534).

As mentioned previously, cracks can develop in the oven wall during coking due to coke expansion. If cracks occur, some raw coke oven gas and the POM it contains can escape to the flue system and be exhausted to the atmosphere via the oven battery combustion exhaust stacks. These stacks are intended only for the exhaust from the fuel burned to provide the heat for coking and not for coke oven gas, which is supposed to be transported to the byproduct recovery portion of the coke plant (57 FR 57534).

At the end of the coking cycle, the product is handled in steps called “pushing” and “quenching.” As depicted in Figure 4.7-1, there are doors at both ends of a coke oven that are removed when coking is finished, and the incandescent coke is pushed out the coke side of the oven by a ram, which is extended from the pusher machine. The coke is pushed through a coke guide into a special railroad car, called a quench car, which traverses the coke side of the battery. The quench car carries the coke to the end of the battery to a quench tower where it is deluged with several thousand gallons of water so that it will not continue to burn after being exposed to air. The quenched coke is discharged onto an inclined coke wharf to allow excess water to drain and the coke to cool to a reasonable handling temperature (U.S. EPA, 1987).

Gates along the lower edge of the wharf control the rate of coke falling on a conveyor belt, which carries the coke to the crushing and screening system. The coke is then crushed and screened to obtain the optimum size for the particular blast furnace operation in which it is to be used. The undersize coke generated by the crushing and screening operations is used in other steel plant processes, stockpiled, or sold (U.S. EPA, 1987).

Coke oven gas and the POM they contain can be released during pushing and quenching due to equipment failure or poor operation. If problems occur in the underfiring system of an oven, or if the oven is pushed out of sequence, or is on an accelerated schedule, the coal may not be completely converted to coke. When this happens, inadequately coked coal (called “green coke”) may be pushed from the oven. Pushing emissions from inadequate coking or green coke are likely to contain POM. These compounds may continue to be emitted when the green coke is quenched with water (57 FR 57534).

Control techniques that have been devised for these operations are listed in Table 4.7-2. These techniques have been implemented to various degrees. Emissions from coke pushing can be controlled by the use of containment/capture and control devices such as hooded, mobile scrubber cars; shed enclosures over the coke side of the battery, evacuated to wet scrubbers or wet ESPs; or traveling hoods with a fixed duct to a stationary gas cleaner. Coke quenching emissions can be controlled mainly through process changes such as the use of single or multiple baffles in the quench tower and the use of only clean water for quenching. Dry quenching may be another option, but this would require additional capture and control devices. Leaks into battery stacks may be controlled through the use of maintenance procedures such as patching cracks in oven walls as needed and containment/capture and control devices such as wet scrubbers, ESPs, or baghouses by which exhaust gases are treated to remove coke oven emissions (Kelly, 1983). The new rule due in 2000 may standardize the use of many of these control techniques and/or mandate the use of others.

Emission Factors

Emission factors for POM from pushing, quenching, and battery stacks developed from available data are given in Tables 4.7-7 and 4.7-8. The quantity and composition of pushing emissions are variable because they depend on the degree of upset to the system. If an oven is pushed out of sequence or before the end of the coking cycle, the green coke will emit more gas and POM than normally expected. The same is true for quenching emissions. The more green coke that is contained in

TABLE 4.7-7. POM EMISSION FACTORS FOR COKE OVENS: PUSHING AND BATTERY STACKS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Range in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-03	Oven Pushing	Uncontrolled	Benz(a)anthracene	4.8E-04 (2.4E-04)	3.1E-04 - 6.5E-04 (1.5E-04 - 3.3E-04)	E
			Benzo(a)pyrene	3.5E-04 (1.7E-04)	2.2E-04 - 4.7E-04 (1.1E-04 - 2.4E-04)	E
			Benzo(b)fluoranthene	4.3E-04 (2.1E-04)	2.7E-04 - 6.8E-04 (1.4E-04 - 2.9E-04)	E
			Benzo(j+k)fluoranthene	3.1E-04 (1.5E-04)	2.0E-04 - 4.2E-04 (9.8E-05 - 2.1E-04)	E
			Chrysene/Triphenylene	5.1E-04 (2.5E-04)	3.3E-04 - 6.9E-04 (1.6E-04 - 3.4E-04)	E
			Dibenz(a,h)anthracene	4.1E-05 (2.0E-05)	2.6E-05 - 5.5E-05 (1.3E-05 - 2.8E-05)	E
			Indeno(1,2,3-cd)pyrene	1.6E-04 (8.1E-05)	1.0E-04 - 2.2E-04 (5.2E-05 - 1.1E-04)	E
			Acenaphthene	3.0E-04 (1.5E-04)	1.9E-04 - 4.0E-04 (9.4E-05 - 2.0E-04)	E
			Acenaphthylene	1.4E-03 (7.1E-04)	9.1E-04 - 1.9E-03 (4.6E-04 - 9.7E-04)	E
			Anthracene	8.6E-04 (4.3E-04)	5.5E-04 - 1.2E-03 (2.7E-04 - 5.8E-04)	E
			Benzo(ghi)perylene	1.5E-04 (7.6E-05)	9.8E-05 -2.1E-04 (4.9E-05 - 1.0E-04)	E
			Fluoranthene	1.6E-03 (7.8E-04)	1.0E-03 - 2.1E-03 (5.0E-04 - 1.1E-03)	E

(continued)

TABLE 4.7-7. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Range in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-03 (continued)	Oven Pushing (continued)	Uncontrolled (continued)	Fluorene	9.8E-04 (4.9E-04)	6.3E-04 - 1.3E-03 (3.1E-04 - 6.6E-04)	E
			Naphthalene	0.017 (8.7E-03)	0.011 - 0.024 (5.6E-03 - 0.012)	E
			Phenanthrene	3.4E-03 (1.7E-03)	2.2E-03 - 4.6E-03 (1.1E-03 - 2.3E-03)	E
			Pyrene	1.1E-03 (5.3E-04)	6.8E-04 - 1.5E-03 (3.4E-04 - 7.3E-04)	E
			1-Methylnaphthalene	7.5E-04 (3.8E-04)	4.8E-04 - 1.0E-03 (2.4E-04 - 5.1E-04)	E
			2-Methylnaphthalene	1.7E-03 (8.5E-04)	1.1E-03 - 2.3E-03 (5.4E-04 - 1.1E-03)	E
			Benzo(a)fluoranthene	8.1E-04 (4.1E-05)	5.2E-05 - 1.1E-04 (2.6E-05 - 5.5E-05)	E
			Benzo(a)fluorene	9.2E-05 (4.6E-05)	5.9E-05 - 1.2E-04 (2.9E-05 - 6.2E-05)	E
			Benzo(e)pyrene	3.3E-04 (1.6E-04)	2.1E-04 - 4.4E-04 (1.0E-04 - 2.2E-04)	E
			Biphenyl	3.8E-04 (1.9E-04)	2.4E-04 - 5.1E-04 (1.2E-04 - 2.6E-04)	E
			Carbazole	1.4E-04 (7.1E-05)	9.1E-05 - 1.9E-04 (4.6E-05 - 9.7E-05)	E
			Coronene	2.0E-05 (1.0E-05)	1.3E-05 - 2.8E-05 (6.5E-06 - 1.4E-05)	E

(continued)

TABLE 4.7-7. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Range in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-03 (continued)	Oven Pushing (continued)	Uncontrolled (continued)	Cyclopenta(cd)pyrene	3.1E-05 (1.5E-05)	2.0E-05 - 4.2E-05 (9.8E-06 - 2.1E-05)	E
			Di- and Trimethylnaphthalenes	1.7E-03 (8.3E-04)	1.1E-03 - 2.2E-03 (5.3E-04 - 1.1E-03)	E
			Dibenzofuran	1.3E-03 (6.6E-04)	8.5E-04 - 1.8E-03 (4.2E-04 - 9.0E-04)	E
			Dibenzothiophene	2.0E-04 (1.0E-04)	1.3E-04 - 2.8E-04 (6.5E-05 - 1.4E-04)	E
			Methyl- and Dimethyldibenzofurans	5.1E-04 (2.6E-04)	3.3E-04 - 6.9E-04 (1.6E-04 - 3.5E-04)	E
			Methylacenaphthylenes	3.0E-04 (1.5E-04)	1.9E-04 - 4.0E-04 (9.4E-05 - 2.0E-04)	E
			Methylbenzfluoranthenes/ Methylbenzpyrene	5.4E-04 (2.7E-04)	3.5E-04 - 7.3E-04 (1.7E-04 - 3.7E-04)	E
			Methylbiphenyls	3.1E-04 (1.5E-04)	2.0E-04 - 4.2E-04 (9.8E-05 - 2.1E-04)	E
			Methylfluorenes	7.0E-04 (3.5E-04)	4.5E-04 - 9.6E-04 (2.2E-04 - 4.8E-04)	E
			Methylphenanthrenes/ Methylanthracenes	5.7E-04 (2.9E-04)	3.6E-04 - 7.8E-04 (1.8E-04 - 3.9E-04)	E
			Perylene	9.2E-05 (4.6E-05)	5.9E-05 - 1.2E-04 (2.9E-05 - 6.2E-05)	E

(continued)

TABLE 4.7-7. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Range in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-06	Oven Underfiring	Uncontrolled	Benz(a)anthracene	6.1E-05 (3.1E-05)[b]	---	E
			Benzo(a)pyrene	4.4E-05 (2.2E-05)[b]	---	E
			Benzo(b)fluoranthene	5.5E-05 (2.7E-05)[b]	---	E
			Benzo(j+k)fluoranthene	3.9E-05 (2.0E-05)[b]	---	E
			Chrysene/Triphenylene	6.5E-05 (3.3E-05)[b]	---	E
			Dibenz(a,h)anthracene	5.2E-06 (2.6E-06)[b]	---	E
			Indeno(1,2,3-cd)pyrene	2.1E-05 (1.0E-05)[b]	---	E
			Acenaphthene	3.8E-05 (1.9E-05)[b]	---	E
			Acenaphthylene	1.8E-04 (9.1E-05)[b]	---	E
			Anthracene	1.1E-04 (5.5E-05)[b]	---	E
			Benzo(ghi)perylene	2.0E-05 (9.8E-06)[b]	---	E
			Fluoranthene	2.0E-04 (1.0E-04)[b]	---	E

(continued)

TABLE 4.7-7. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Range in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-06 (continued)	Oven Underfiring (continued)	Uncontrolled (continued)	Fluorene	1.3E-04 (6.3E-05)[b]	---	E
			Naphthalene	2.2E-03 (1.1E-03)[b]	---	E
			Phenanthrene	4.4E-04 (2.2E-04)[b]	---	E
			Pyrene	1.4E-04 (6.8E-05)[b]	---	E
			1-Methylnaphthalene	9.6E-05 (4.8E-05)[b]	---	E
			2-Methylnaphthalene	2.2E-04 (1.1E-04)[b]	---	E
			Benzo(a)fluoranthene	1.0E-05 (5.2E-06)[b]	---	E
			Benzo(a)fluorene	1.2E-05 (5.9E-06)[b]	---	E
			Benzo(e)pyrene	4.2E-05 (2.1E-05)[b]	---	E
			Biphenyl	4.8E-05 (2.4E-05)[b]	---	E
			Carbazole	1.8E-05 (9.1E-06)[b]	---	E
			Coronene	2.6E-06 (1.3E-06)[b]	---	E

(continued)

TABLE 4.7-7. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Range in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-03-003-06 (continued)	Oven Underfiring (continued)	Uncontrolled (continued)	Cyclophenta(cd)pyrene	3.9E-06 (2.0E-06)[b]	---	E
			Di- and Trimethylnaphthalenes	2.1E-04 (1.1E-04)[b]	---	E
			Dibenzofuran	1.7E-04 (8.5E-05)[b]	---	E
			Dibenzothiophene	2.6E-05 (1.3E-05)[b]	---	E
			Methyl- and Dimethyldibenzofurans	6.5E-05 (3.3E-05)[b]	---	E
			Methylacenaphthylenes	3.8E-05 (1.9E-05)[b]	---	E
			Methylbenzfluoranthenes/ Methylbenzpyrene	6.9E-05 (3.5E-05)[b]	---	E
			Methylbiphenyls	3.9E-05 (2.0E-05)[b]	---	E
			Methylfluorenes	9.0E-05 (4.5E-05)[b]	---	E
			Methylphenanthrenes/ Methylanthracenes	7.3E-05 (3.6E-05)[b]	---	E
			Perylene	1.2E-05 (5.9E-06)[b]	---	E

[a] Emission factors in lb/ton (kg/Mg) of coal charged.
[b] POM leaks are transported to the battery stacks through the oven underfiring system.

Source: Trenholm and Beck, 1978; Kirton and Crisp, 1991.

TABLE 4.7-8. POM EMISSION FACTORS FOR COKE OVENS: QUENCHING

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton[a] (kg/Mg)	Emission Factor Rating
3-03-003-04	Quenching - Nongreen Coke	Uncontrolled	Benz(a)anthracenes/Chrysene	1.3E-04 (6.5E-05)[b]	D
			Benzo(a)pyrene	6.5E-04 (3.2E-04)[b]	D
			Benzofluoranthene/Benzo(e)pyrene	1.6E-04 (7.8E-05)[b]	D
			Indeno(1,2,3-cd)pyrene	6.6E-06 (3.3E-06)[b]	D
			Acenaphthene/Biphenyl	5.5E-04 (2.8E-04)[b]	D
			Acenaphthylene/Biphenylene	5.5E-03 (2.7E-03)[b]	D
			Anthracene/Phenanthrene	6.9E-03 (3.5E-03)[b]	D
			Fluoranthene	1.5E-03 (7.6E-04)[b]	D
			Fluorene	4.8E-03 (2.4E-03)[b]	D
			Naphthalene	0.033 (0.017)[b]	D
			Pyrene	1.4E-03 (7.1E-04)[b]	D
			3-Methylcholanthrene	1.2E-05 (5.9E-06)[b]	D

(continued)

TABLE 4.7-8. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton[a] (kg/Mg)	Emission Factor Rating
3-03-003-04 (continued)	Quenching - Nongreen Coke (continued)	Uncontrolled (continued)	Benzothiophene	1.7E-03 (8.6E-04)[b]	D
			$C_{16}H_{12}$ PAH	9.3E-05 (4.7E-05)[b]	D
			$C_{16}H_{16}$ PAH	2.4E-05 (1.2E-05)[b]	D
			Carbazole	8.1E-04 (4.1E-04)[b]	D
			Dibenzofuran/Methylbiphenyl	2.1E-03 (1.0E-03)[b]	D
			Dibenzothiophene	3.5E-04 (1.7E-04)[b]	D
			Dihydrobenzofluorene	8.8E-05 (4.4E-05)[b]	D
			Dimethylnaphthalenes	5.3E-04 (2.7E-04)[b]	D
			Indene	2.8E-04 (1.4E-04)[b]	D
			Methylanthracenes	6.1E-04 (3.0E-04)[b]	D
			Methylchrysenes	2.2E-05 (1.1E-05)[b]	D
			Methylfluoranthenes/Methylpyrenes	1.9E-04 (9.5E-05)[b]	D

(continued)

TABLE 4.7-8. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton[a] (kg/Mg)	Emission Factor Rating
3-03-003-04 (continued)	Quenching - Nongreen Coke (continued)	Uncontrolled (continued)	Methylnaphthalenes	2.9E-03 (1.4E-03)[b]	D
			Naphthobenzothiophene	5.3E-06 (2.6E-06)[b]	D
			Perylene	4.6E-05 (2.3E-05)[b]	D
3-03-003-04	Quenching - Nongreen Coke	Clean Water	Benz(a)anthracenes/Chrysene	2.8E-05 (1.4E-05)	D
			Benzo(a)pyrene	2.0E-04 (9.8E-05)	D
			Indeno (1,2,3-cd)pyrene	3.6E-06 (1.8E-06)	D
			Acenaphthene/Biphenyl	4.7E-06 (2.3E-06)	D
			Acenaphthylene/Biphenylene	1.4E-05 (6.8E-06)	D
			Anthracene/Phenanthrene	1.9E-04 (9.7E-05)	D
			Benzo(ghi)perylene	2.4E-05 (1.2E-05)	D
			Fluoranthene	6.2E-05 (3.1E-05)	D
			Fluorene	3.2E-05 (1.6E-05)	D

(continued)

TABLE 4.7-8. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton[a] (kg/Mg)	Emission Factor Rating
3-03-003-04 (continued)	Quenching - Nongreen Coke (continued)	Clean Water (continued)	Naphthalene	2.0E-04 (1.0E-04)	D
			Pyrene	2.6E-05 (1.3E-05)	D
			3-Methylcholanthrene	2.1E-05 (1.1E-05)	D
			Benzothiophene	1.1E-06 (5.3E-07)	D
			$C_{16}H_{12}$ PAH	2.6E-06 (1.3E-06)	D
			Dibenzofuran/Methylbiphenyl	1.6E-05 (7.9E-06)	D
			Dibenzothiophene	8.2E-06 (4.1E-06)	D
			Dihydrobenzofluorene	2.3E-05 (1.1E-05)	D
			Dimethylnaphthalenes	3.3E-05 (1.6E-05)	D
			Methylanthracenes	9.0E-05 (4.5E-05)	D
			Methylfluoranthenes/Methylpyrenes	7.3E-06 (3.7E-06)	D
			Methylnaphthalenes	4.7E-05 (2.3E-05)	D

(continued)

TABLE 4.7-8. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton[a] (kg/Mg)	Emission Factor Rating
3-03-003-04	Quenching - Green Coke	Clean Water	Benz(a)anthracenes/Chrysene	9.4E-06 (4.7E-06)	D
			Benzo(a)pyrene	9.7E-05 (4.9E-05)	D
			Acenaphthene/Biphenyl	2.7E-05 (1.4E-05)	D
			Acenaphthylene/Biphenylene	9.8E-05 (4.9E-05)	D
			Anthracene/Phenanthrene	4.5E-04 (2.3E-04)	D
			Fluoranthene	1.2E-04 (5.9E-05)	D
			Fluorene	9.6E-05 (4.8E-05)	D
			Naphthalene	5.1E-04 (2.6E-04)	D
			Pyrene	1.3E-04 (6.6E-05)	D
			3-Methylcholanthrene	2.0E-05 (9.8E-06)	D
			Benzothiophene	1.6E-06 (8.0E-07)	D
			Dibenzofuran/Methylbiphenyl	8.0E-05 (4.0E-05)	D

(continued)

TABLE 4.7-8. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton[a] (kg/Mg)	Emission Factor Rating
3-03-003-04 (continued)	Quenching - Green Coke (continued)	Clean Water (continued)	Dibenzothiophene	3.8E-06 (1.9E-06)	D
			Dihydrobenzofluorene	2.3E-05 (1.2E-05)	D
			Dimethylnaphthalenes	3.3E-04 (1.6E-04)	D
			Methylanthracenes	3.1E-04 (1.5E-04)	D
			Methylfluoranthenes/Methylpyrenes	6.3E-05 (3.2E-05)	D
			Methylnaphthalenes	1.9E-04 (9.4E-05)	D
			Perylene	3.1E-05 (1.5E-05)	D

[a] Emission factors in lb/ton (kg/Mg) of coal charged.
[b] Contaminated water used for quenching.

Source: Laube and Drummond, 1979.

the product, the greater the quantity of emissions liberated during quenching. Finally, the quantity of leaks into the combustion exhaust stacks at any given plant will vary; it is difficult to establish an emission factor for battery stacks although the emissions are still considered significant enough to warrant control.

Because the focus of regulatory efforts has been on the initial charging operation and door and topside leaks, little new data has been developed regarding emissions from pushing, quenching, and battery stacks. Only one report (Trenholm and Beck, 1978) documented BSO emissions from pushing. Individual POM emission factors for pushing were derived from the BSO emission factor shown in Table 4-7-4 using the speciation profile in Table 4.7-1. Likewise, this report was the only one to report BSO emissions from battery stacks, and the individual PAH emission factors were derived from this single piece of data. Therefore, caution is again recommended in the use of these emission factors.

Of these three emission points, the most attention has been paid to the quenching operation because at one time, it was suspected as being the most significant POM emission source after door leaks. In one test program (Laube and Drummond, 1979), the effect of using clean versus contaminated (reused) quench water as a control technique was evaluated. The tests indicated that the use of clean quench water reduced total PAH emissions by about 95 percent. This finding spurred further investigation of this particular control technique yielding somewhat similar results (Johnson et al., 1990).

The first test program investigating quenching emissions was undertaken in support of Federal rule development, and individual PAH were analyzed, the data from which can be used to develop emission factors. The test program indicated that benzo(a)pyrene emissions from quenching were much less than from the other coke oven points. This may be due to the time in the coking cycle that quenching takes place, i.e., most volatiles have been driven off the coal by the time it has been coked and is ready to be quenched. Thus, the average BSO speciation profile used for the other coke oven points may not be the best indication of the individual PAH composition of emissions from quenching. Hence, the PAH emission factors for quenching have been developed from this single test program (Laube and Drummond, 1979), not from the BSO emission factor shown in Table 4.7-4.

The use of baffles as a control technique in the quenching operation targets particulate emissions, not POM *per se*, but because POM is often associated with particulate matter, the use of baffles still qualifies as a POM control technique. Tests indicate that baffles can reduce total particulate by 50 to 75 percent.

Even when a particular control technique is in place, the variability in the quantity and composition of coke oven emissions from quenched coke makes it impossible to establish an accurate overall emission factor. Hence, as with pushing and battery stack emissions, a range of emission factors from quenching is provided, which is derived from BSO emission factors that have been reported. Because this range encompasses the values for emission factors from other reports of emissions of total PAH or benzo(a)pyrene, the other reports are not included separately.

Source Locations

Pushing and quenching operations are carried out and battery stacks are located at all of the coke oven plants listed in Table 4.7-5.

4.7.3 Coke Byproduct Recovery Plants

Process Description

Volatile components that are driven off the coal during coking are transported to the byproduct recovery portion of coke plants fitted with such operations. Coke oven gas that has not leaked out leaves the coke oven battery through standpipes, passes into goosenecks, and travels through a damper valve to the gas collection main, which directs it to the byproduct recovery plant. This gas accounts for 20 to 35 percent by weight of the initial coal charge and is composed of water vapor, tar, light oils, heavy hydrocarbons, and other chemical compounds, including POM (U.S. EPA, 1987).

Following the process flow diagram in Figure 4.7-2, raw coke oven gas exits the ovens at temperatures of 1,400 to 1,600°F (760 to 870°C) and is shock-cooled by spraying recycled flushing liquor in the gooseneck. This spray cools the gas to 180 to 210°F (80 to 100°C), precipitates tar, condenses various vapors, and serves as the carrying medium for the condensed compounds. These products are separated from the liquor in a decanter and are subsequently processed to yield tar and tar derivatives. The gas is then passed either to a final tar extractor or an electrostatic precipitator for additional tar removal. When the gas leaves the tar extractor, it carries 75 percent of the ammonia and 95 percent of the light oil originally present when leaving the oven (U.S. EPA, 1987).

The ammonia is recovered either as an aqueous solution by water absorption or as ammonium sulfate salt. Ammonium sulfate is crystallized in a saturator, which contains a solution of 5 to 10 percent sulfuric acid and is removed by an air injector or centrifugal pump. The salt is dried in a centrifuge and packaged. The ammonia-stripped gas leaving the saturator at about 140°F (60°C) is taken to final coolers or condensers, where it is typically cooled with water to approximately 75°F (24°C). During this cooling, much of the naphthalene separates and is carried along with the wastewater and recovery (U.S. EPA, 1987).

After naphthalene is removed, the remaining gas is passed into a light oil or benzol scrubber, over which is circulated a heavy petroleum fraction called wash oil or a coal-tar oil that serves as the absorbent medium. The oil is sprayed in the top of the packed absorption tower while the gas flows up through the tower. The wash oil absorbs about 2 to 3 percent of its weight of light oil, with a removal efficiency of about 95 percent of the light oil vapor in the gas. The rich wash oil is passed to a countercurrent steam stripping column. The steam and light oil vapors pass upward from the still through a heat exchanger to a condenser and water separator. The light oil may be sold as crude or processed to recover benzene, toluene, xylene, and solvent naphtha (U.S. EPA, 1987).

After tar, ammonia, and light oil removal, the gas undergoes a final desulfurization process at some coke plants before being used as fuel. The “clean” coke oven gas has a rather high heating value, on the order of 550 Btu/stdft^3 (20 MJ/Nm^3). Typically, 35 to 40 percent of the gas is returned to fuel the coke oven combustion system, and the remainder is used for other plant heating needs (U.S. EPA, 1987).

The points emitting the highest POM concentrations in byproduct recovery plants are the tar decanter, tar dewatering and storage, tar distillation products, naphthalene separator, and final-cooler cooling tower. The data suggest that POM accumulates as a concentrate in liquified streams (tars, flushing liquor, tar products, wash and wastewaters), and can be emitted when the streams are processed or used, such as when recycled water from the final cooler passes through the open cooling tower. Naphthalene was identified as being the POM emitted in the greatest quantity (Van Osdell, 1979).

As mentioned previously, benzene emissions from the byproduct recovery portion of coke plants are now regulated. The nature of the controls required by a benzene NESHAP promulgated in 1989 have the effect of controlling much of the POM emissions from the plant as well because POM and benzene are emitted from many of the same points. The benzene emission control techniques that also control POM are described next.

Gas blanketing with clean coke oven gas from the gas holder (or battery underfire system) is the control technology required by the 1989 benzene NESHAP for tar processing (54 FR 38044). With this technology, the different tar processing points are enclosed and a positive (or negative) pressure blanket of clean coke oven gas is piped in. Using a series of piping connections and flow inducing devices (if necessary), vapor emissions from the enclosed sources are transported back into the clean gas system (the coke-oven battery holder, the collecting main, or another point in the byproduct recovery process). Ultimate control of the vapors (benzene and all other emissions) is accomplished by the combustion of the coke oven gas (U.S. EPA, 1984).

Such systems are currently in use at some byproduct recovery plants and reportedly have operated without difficulty. Examples of gases that may be used as the gas blanket include dirty or clean coke gas, nitrogen, or natural gas (U.S. EPA, 1984). The control efficiency for benzene is estimated to be 98 percent except for the tar decanter, where the efficiency is estimated to be 95 percent. The control efficiency for POM can be assumed to be the same or better because POM is less volatile than benzene; hence less of it should escape the blanketing system.

The 1989 benzene NESHAP requires that all benzene emissions from naphthalene processing, final coolers, and final-cooler cooling towers be eliminated (54 FR 38044). The available controls, which reduce all emissions including POM to zero, are conversion to a different type of cooling tower or elimination of the cooling tower. A facility with a direct-water final cooler could insert a one-stage mixer-settler into the final cooling process and thus obtain the benefits of a tar-bottom cooler. Although a tar-bottom cooler does not eliminate emissions from the cooling tower, it does eliminate emissions associated with the physical separation of naphthalene and water. Alternatively, the facility could convert to a wash oil final cooler, which effectively eliminates the emissions associated with direct water or tar-bottom coolers because the wash oil is cooled by an indirect heat exchanger, thereby eliminating the need for a cooling tower. Wash oil is separated after it leaves the heat exchanger and recirculates back through the circulation tank to the final cooler (U.S. EPA, 1984).

Emission Factors

Emissions of pollutants other than benzene from byproduct recovery plants have been investigated fairly extensively in support of Federal rule development. Values of total POM are available; however, little attempt has been made to speciate POM fully. This is due first to the recognition that, once again, the composition of POM is variable, and second to the finding that because so much of the POM emissions is naphthalene, the remaining species could be considered insignificant (VanOsdell et al., 1979).

It should be noted that naphthalene is the only constituent of POM that is a commercially desirable chemical product. As such, emissions of naphthalene resulting from its production and use are discussed separately in Section 5.0 of this document. The principal method of producing naphthalene is in the coke byproduct recovery step of coke production; the naphthalene recovery portion of the coke byproduct recovery operation is described in greater detail in Section 5.0.

Finally, the 1989 benzene NESHAP required full implementation by three years from promulgation, so it can be assumed that data collected previously to support regulatory development no longer reflect the reduced emissions from this source today. Hence, no emission factors are presented for this portion of the byproduct coking process other than the naphthalene emission factors presented in Section 5.0. Overall, before promulgation of the 1989 benzene NESHAP, emissions of POM from the byproduct recovery process were estimated to be 23 tpy (21 Mg/yr). The estimated impact of the 1989 NESHAP is a reduction in benzene emissions of 93 percent and a reduction in overall VOC, including POM of 96 percent (U.S. EPA, 1988).

Source Locations

All of the coke oven plants listed in Table 4.7-5 are designed to recover coke byproducts and have byproduct recovery plants co-located with them. In 1994 there was one nonrecovery plant operating in the U.S. (in Vansant, Virginia). As the name implies, this process does not recover the numerous chemical byproducts as discussed in the previous section. All of the coke oven gas is burned, and instead of recovery of chemicals, this process offers the potential for heat recovery and cogeneration of electricity. The plant that is currently operating does not have waste heat recovery; however, any new construction of this process at integrated iron and steel plants is expected to take advantage of the economic incentives of recovering the waste heat (U.S. EPA, 1995).

SECTION 4.7 REFERENCES

Federal Register. National Emission Standards for Hazardous Air Pollutants; Benzene Emissions from Maleic Anhydride Plants, Ethylbenzene/Styrene Plants, Benzene Storage Vessels, Benzene Equipment Leaks, and Coke By-Product Recovery Plants. Volume 54, No. 177, p. 38044 (54 FR 38044) September 14, 1989.

International Agency for Research on Cancer (IARC). Volume 34: Polynuclear Aromatic Compounds, Part 3. Industrial Exposures in Aluminum Production, Coal Gasification, Coke Production, and Iron and Steel Founding. IARC Press, 150 cours Albert Thomas, F-69372 Lyon Cedex 08, France. ISBN 92 832 15346. 1984.

Johnson, N.D. et al. MOE Toxic Chemical Emissions 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. 1990.

Kelly, M.E. Sources and Emissions of Polycyclic Organic Matter. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA-450/5-83-010b. 1983.

Kirton, P.J., J. Ellis, and P.T. Crisp. “The Analysis of Organic Matter in Coke Oven Emissions.” Fuel, Volume 70, pp. 1383-1389. 1991.

Laube, A.H., and B.A. Drummond. Coke Quench Tower Emission Testing Program (Draft). Prepared for Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA Contract No. 68-02-2819. 1979.

Trenholm, A.R., and L.L. Beck. Assessment of Hazardous Organic Emissions from Slot Type Coke Oven Batteries. U.S. Environmental Protection Agency, Emission Standards and Engineering Division, Research Triangle Park, North Carolina. 1978.

U.S. Environmental Protection Agency. Compilation of Air Pollution Emission Factors - AP-42, Draft Section 12.2: Coke Production. 1995.

U.S. Environmental Protection Agency. Benzene Emissions from Coke Byproduct Recovery Plants - Background Information for Revised Proposed Standards. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/3-83-016b. 1988.

U.S. Environmental Protection Agency. Coke Oven Emissions from Wet-Coal Charged Byproduct Coke Oven Batteries - Background Information for Proposed Standards. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/3-85-028a. April 1987.

U.S. Environmental Protection Agency. Benzene Emissions from Coke Byproduct Recovery Plants - Background Information for Proposed Standards. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/3-83-016a. May 1984.

VanOsdell, D.W., D. Marsland, B.H. Carpenter, C. Sparacino, and R. Jablin. Environmental Assessment of Coke Byproduct Recovery Plants. Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA-600/2-79-016. 1979.

4.8 PORTLAND CEMENT MANUFACTURING

Most of the hydraulic cement produced in the United States is portland cement, a crystalline compound composed of metallic oxides. Raw materials used in the process can be limestone that contains calcium carbonate and aluminum, iron, and silicon oxides, shale, clay, and sand (U.S. EPA, 1995). There are four primary components in portland cement manufacturing: raw materials handling, kiln feed preparation, pyroprocessing, and finished cement grinding. Pyroprocessing, the fuel-intensive process accomplished in cement kilns, has been identified as a potential source of POM emissions, and constitutes the primary focus of this chapter.

Process Description

Typically, most raw materials used in portland cement manufacturing are quarried on site and transferred by conveyor to crushers and raw mills. After the raw materials are reduced to the desired particle size, they are blended and fed to a large rotary kiln (RTI, 1994).

There are five variations in portland cement manufacturing: wet, dry, semidry, dry with a preheater, and dry preheater/precalciner processes. These processes are essentially identical in their raw materials and end product. However, the type of process does affect the equipment design, method of operation, and fuel consumption. In the first three, all fuel combustion occurs in the kiln. In the latter two, some fuel combustion occurs in a precalcining or calcining vessel before the materials enter the kiln.

In general, fuel consumption decreases in the order of the processes listed above. The preheater/precalciner equipment uses less fuel and requires a shorter kiln, and the wet process uses the most fuel and requires the longest kiln, but the relationship is not linear (U.S. EPA, 1995). Many older kilns use the wet process; in the past, wet grinding and mixing technologies provided more uniform and consistent material mixing, resulting in a higher quality clinker. Technologies have improved, however, to the point that all of the new kilns since 1975 use the dry process (U.S. EPA, 1991).

The kiln system for the manufacture of portland cement by dry process with preheater is shown in Figure 4.8-1. The raw material enters a four-stage suspension preheater, where hot gases from the kiln heat the raw feed and provide about 40 percent calcination (Stream 1) before the feed enters the kiln. Some installations include a precalcining furnace (Stream 2), which provides about 85 percent calcination before the feed enters the kiln (U.S. EPA, 1995).

The feed enters the kiln at the elevated end, and the burner is located at the opposite end. The raw materials are then changed into cementitious oxides of metal by a countercurrent heat exchange process. The materials are continuously and slowly moved to the low end by the rotation of the kiln while being heated to temperatures of approximately 2,700°F (1,480°C) by direct firing (Stream 3). In this stage, chemical reactions occur, and a rock-like substance called “clinker” is formed. This clinker is then cooled, crushed, and blended with gypsum to produce portland cement (U.S. EPA, 1995). The cement is then either bagged or bulk-loaded and transported out (RTI, 1994).

Portland cement production is a fuel-intensive process. The fuel burned in the kiln may be natural gas, oil, or coal. Many cement plants burn coal, but supplemental fuels such as waste solvents, chipped rubber or tire-derived fuel (TDF), shredded municipal garbage, and coke have been used in recent years (U.S. EPA, 1995). A major trend in the industry is the increased use of hazardous waste-derived fuels (HWDFs). In 1989, 33 plants in the United States and Canada reported using waste fuels; that number increased to 55 plants in 1990 (U.S. EPA, 1995).

The increased use of HWDFs is attributed to lower cost and increased availability. As waste generators reduce or eliminate solvents from their waste steams, the streams will contain more sludge and solids.

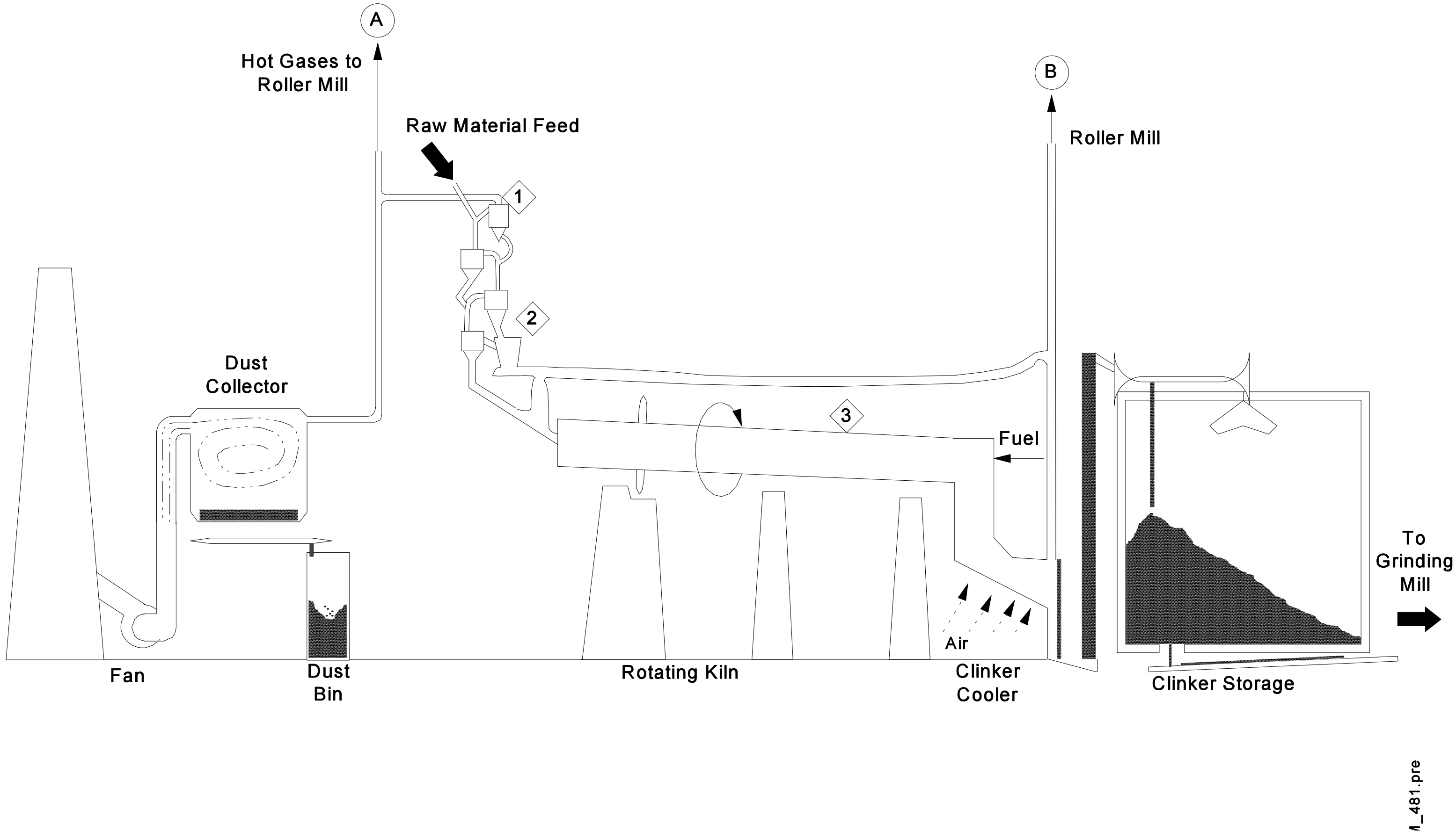


Figure 4.8-1. Process Diagram of Portland Cement Manufacturing by Dry Process with Preheater

Source: U.S. EPA, 1995.

Facilities that burn HWDFs are subject to the Boilers and Industrial Furnaces (BIF) rule under the Resource Conservation and Recovery Act (RCRA) promulgated February 21, 1991. The BIF rule requires that a facility that burns hazardous waste demonstrate a 99.99-percent destruction efficiency for principal organic hazardous constituents in the waste stream. To guard against products of incomplete combustion, the BIF rule limits CO levels in the kiln or total hydrocarbon levels in the stack gases (Kim, 1994; U.S. EPA, 1994). Maximum achievable control technology (MACT) Standards are being developed for BIFs under the joint authority of RCRA and the Clean Air Act (CAA). The MACT Standards will apply to the following three BIF source categories: hazardous waste incinerators, cement kilns that burn hazardous waste, and light weight aggregate kilns that burn hazardous waste (Behan Telecon, 1995).

Emission Factors

The raw materials used by some facilities may contain organic compounds and thus be the source of POM emissions during the heating step. However, fuel combustion to heat the kiln is believed to be the primary source of POM emissions. The data collected and presented in this chapter indicate that POM is emitted from portland cement kilns firing fossil fuels, waste fuels, HWDFs, and combinations of the above (U.S. EPA, 1995; U.S. EPA, 1994).

PAH emissions data for portland cement kilns with various process, fuel, and control configurations were compiled by the Office of Solid Waste (OSW) in 1994 and the Office of Air Quality Planning and Standards (OAQPS) in 1991 and 1994 (U.S. EPA, 1994; U.S. EPA, 1991; U.S. EPA, 1995). The OSW document reports results of tests conducted at 35 portland cement manufacturing facilities to certify compliance with the BIF rule. PAH emission factors were derived from the OSW report when sufficient emissions and process information were available. Emission factors were presented in the two additional EPA reports based on test data from two individual facilities (U.S.EPA, 1991; U.S. EPA, 1995).

Wet process cement kiln PAH emission factors are presented in Tables 4.8-1 through 4.8-8. Table 4.8-1 lists emission factors from a coal/liquid and solid hazardous waste-fired cement kiln equipped with an electrostatic precipitator (ESP). During testing, the kiln was operated at low combustion temperature and high hazardous waste feed. Table 4.8-2 contains emission factors from a coal/coke/liquid and solid hazardous waste-fired cement kiln equipped with ESP. During testing, the kiln was operated at high combustion temperature and high hazardous waste feed. Table 4.8-3 lists emission factors from a liquid and solid waste-fired cement kiln equipped with an ESP and operated at low combustion temperature and high hazardous waste feed.

Table 4.8-4 lists emission factors from a natural gas/hazardous waste-fired cement kiln equipped with an ESP and operated at low combustion temperature. Table 4.8-5 contains emission factors from a coal/coke-fired cement kiln equipped with an ESP and operated at high combustion temperature. Table 4.8-6 contains emission factors from a coal/coke/liquid hazardous waste-fired cement kiln equipped with an ESP and operated a low combustion temperature with high hazardous waste feed. Tables 4.8-7 and 4.8-8 list emission factors from a single ESP-equipped cement kiln under two fuel scenarios: 100 percent coal firing and 14 percent TDF/86 percent coal firing, respectively.

Dry and dry precalciner process cement kiln PAH emission factors are presented in Tables 4.8-9 through 4.8-12. Table 4.8-9 lists emission factors for a coal/coke/liquid and solid hazardous waste-fired dry process cement kiln equipped with an ESP and operated at low combustion temperature and high hazardous waste feed. Table 4.8-10 lists emission factors from a coke/hazardous waste-fired dry process cement kiln equipped with a multiclyclone and ESP in series and operated at high combustion temperature and high hazardous waste feed. Table 4.8-11 lists emission factors from a coal/hazardous waste-fired dry process cement kiln equipped with a fabric filter. Table 4.8-12 contains emission factors from a coal-fired dry precalciner process cement kiln equipped with a fabric filter.

TABLE 4.8-1. PAH EMISSION FACTORS FOR COAL/HAZARDOUS WASTE-FIRED WET PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-007-6	Wet Process Cement Kiln	Electrostatic Precipitator	Benz(a)anthracene	3.23E-05 (1.62E-05)	D
			Benzo(b)fluoranthene	4.65E-05 (2.33E-05)	D
			Chrysene	6.79E-05 (3.39E-05)	D
			Acenaphthylene	3.45E-04 (1.73E-04)	D
			Fluorene	3.88E-05 (1.94E-05)	D
			Fluoranthene	2.22E-04 (1.11E-04)	D
			Naphthalene	9.07E-04 (4.53E-04)	D
			Phenanthrene	3.44E-04 (1.72E-04)	D
			Pyrene	6.95E-04 (3.47E-04)	D
			2-Methylnaphthalene	7.13E-05 (3.56E-05)	D

[a] Kiln operating conditions: low combustion temperature; high liquid and solid hazardous waste feed.
[b] Emission factors are in lb/kg of pollutant emitted per ton (Mg) of clinker produced.

Source: U.S. EPA, 1994.

TABLE 4.8-2. PAH EMISSION FACTORS FOR COAL/COKE/HAZARDOUS WASTE-FIRED WET PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-007-6	Wet Process Cement Kiln	Electrostatic Precipitator	Benzo(b)fluoranthene	1.33E-05 (6.67E-06)	D
			Chrysene	5.85E-06 (2.92E-06)	D
			Acenaphthylene	2.59E-04 (1.30E-04)	D
			Anthracene	1.76E-05 (8.81E-06)	D
			Fluorene	2.22E-05 (1.11E-05)	D
			Fluoranthene	1.33E-04 (6.66E-05)	D
			Naphthalene	8.22E-04 (4.11E-04)	D
			Phenanthrene	2.26E-04 (1.13E-04)	D
			Pyrene	7.55E-05 (3.78E-05)	D
			2-Methylnaphthalene	7.07E-05 (3.54E-05)	D

[a] Kiln operating conditions: low combustion temperature; high liquid and solid hazardous waste feed.
[b] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of clinker produced.

Source: U.S. EPA, 1994.

TABLE 4.8-3. PAH EMISSION FACTORS FOR HAZARDOUS WASTE-FIRED WET PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-007-6	Wet Process Cement Kiln	Electrostatic Precipitator	Acenaphthylene	3.76E-05 (1.88E-05)	C
			Fluoranthene	3.10E-05 (1.55E-05)	C
			Naphthalene	8.01E-04 (4.01E-04)	C
			Phenanthrene	1.71E-04 (8.54E-05)	C
			Pyrene	2.18E-05 (1.09E-05)	C
			2-Methylnaphthalene	1.68E-04 (8.39E-05)	C

[a] Kiln operating conditions: low combustion temperature; high liquid and solid hazardous waste feed.
[b] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of clinker produced.

Source: U.S. EPA, 1994.

TABLE 4.8-4. PAH EMISSION FACTORS FOR GAS/HAZARDOUS WASTE-FIRED WET PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-007-6	Wet Process Cement Kiln	Electrostatic Precipitator	Acenaphthylene	1.20E-04 (6.02E-05)	D
			Anthracene	5.92E-06 (2.96E-06)	D
			Fluorene	4.66E-06 (2.33E-06)	D
			Fluoranthene	3.99E-05 (1.99E-05)	D
			Naphthalene	7.28E-04 (3.64E-04)	D
			Phenanthrene	1.45E-04 (7.26E-05)	D
			Pyrene	3.07E-05 (1.53E-05)	D
			2-Methylnaphthalene	6.42E-04 (3.21E-04)	D

[a] Kiln operating conditions: low combustion temperature; liquid and solid hazardous waste firing.
[b] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of clinker produced.

Source: U.S. EPA, 1994.

TABLE 4.8-5. PAH EMISSION FACTORS FOR COAL/COKE-FIRED WET PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-007-6	Wet Process Cement Kiln	Electrostatic Precipitator	Benz(a)anthracene	7.24E-05 (3.62E-05)	D
			Benzo(a)pyrene	2.73E-05 (1.37E-05)	D
			Benzo(b)fluoranthene	3.21E-06 (1.61E-06)	D
			Chrysene	1.32E-04 (6.61E-05)	D
			Dibenz(a,h)anthracene	3.21E-06 (1.61E-06)	D
			Indeno(1,2,3-cd)pyrene	4.51E-06 (2.25E-06)	D
			Acenaphthene	7.84E-05 (3.92E-05)	D
			Acenaphthylene	5.18E-04 (2.59E-04)	D
			Anthracene	1.63E-04 (8.16E-05)	D
			Benzo(ghi)perylene	3.21E-06 (1.61E-06)	D
			Fluorene	3.02E-04 (1.51E-04)	D
			Fluoranthene	2.17E-04 (1.09E-04)	D

(continued)

TABLE 4.8-5. (Continued)

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-007-6 (continued)	Wet Process Cement Kiln (continued)	Electrostatic Precipitator (continued)	Naphthalene	9.66E-04 (4.83E-04)	D
			Phenanthrene	6.01E-04 (3.01E-04)	D
			Pyrene	1.61E-04 (8.06E-05)	D
			2-Methylnaphthalene	1.01E-03 (5.05E-04)	D

[a] Kiln operating conditions: high combustion temperature.
[b] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of raw material slurry input.

Source: U.S. EPA, 1994.

TABLE 4.8-6. PAH EMISSION FACTORS FOR COAL/COKE/HAZARDOUS WASTE-FIRED WET PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-007-6	Wet Process Cement Kiln	Electrostatic Precipitator	Benz(a)anthracene	1.56E-04 (7.80E-05)	D
			Benzo(a)pyrene	7.92E-05 (3.96E-05)	D
			Benzo(b)fluoranthene	4.61E-05 (2.30E-05)	D
			Chrysene	2.76E-04 (1.38E-04)	D
			Dibenz(a,h)anthracene	1.43E-05 (7.13E-06)	D
			Indeno(1,2,3-cd)pyrene	1.74E-05 (8.68E-06)	D
			Acenaphthene	1.24E-04 (6.18E-05)	D
			Acenaphthylene	8.32E-04 (4.16E-04)	D
			Anthracene	3.21E-04 (1.60E-04)	D
			Benzo(ghi)perylene	3.33E-05 (1.67E-05)	D
			Fluorene	9.51E-04 (4.75E-04)	D
			Fluoranthene	3.49E-04 (1.74E-04)	D

(continued)

TABLE 4.8-6. (Continued)

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-007-6 (continued)	Wet Process Cement Kiln (continued)	Electrostatic Precipitator (continued)	Naphthalene	9.99E-04 (5.00E-04)	D
			Phenanthrene	9.07E-04 (4.54E-04)	D
			Pyrene	1.24E-04 (6.20E-05)	D
			2-Methylnaphthalene	1.19E-03 (5.94E-04)	D

[a] Kiln operating conditions: low combustion temperature; liquid hazardous waste feed.
[b] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of raw material slurry input.

Source: U.S. EPA, 1994.

TABLE 4.8-7. PAH EMISSION FACTORS FOR COAL-FIRED WET PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ)[a]	Emission Factor Rating
3-05-007-6	Wet Process Cement Kiln	Electrostatic Precipitator	Benzo(a)pyrene	2.04E-06 (8.77E-07)	D
			Acenaphthene	2.76E-06 (1.19E-06)	D
			Acenaphthylene	2.20E-07 (9.46E-08)	D
			Anthracene	2.46E-06 (1.06E-06)	D
			Fluorene	7.65E-06 (3.29E-06)	D
			Naphthalene	3.40E-04 (1.46E-04)	D
			Pyrene	4.97E-06 (2.14E-06)	D
			Benz(b)anthracene	9.88E-06 (4.25E-06)	D
			Dibenz(g,h)anthracene	1.07E-04 (4.59E-05)	D

[a] Emission factors are in lb (g) of pollutant emitted per MMBtu (MJ) of heat input.

Source: U.S. EPA, 1991.

TABLE 4.8-8. PAH EMISSION FACTORS FOR COAL/TDF-FIRED WET PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ)[b]	Emission Factor Rating
3-05-007-6	Wet Process Cement Kiln	Electrostatic Precipitator	Acenaphthene	2.06E-06 (8.86E-07)	D
			Benzo(ghi)perylene	1.03E-05 (4.44E-06)	D
			Fluorene	7.12E-06 (3.06E-06)	D
			Naphthalene	1.59E-04 (6.84E-05)	D
			Pyrene	2.23E-06 (9.59E-07)	D
			Dibenz(g,h)anthracene	6.72E-05 (2.89E-05)	D

[a] Kiln fuel scenario: 86 percent coal - 14 percent tire derived fuel (TDF).
[b] Emission factors are in lb (g) of pollutant emitted per MMBtu (MJ) of heat input.

Source: U.S. EPA, 1991.

TABLE 4.8-9. PAH EMISSION FACTORS FOR COAL/COKE/HAZARDOUS WASTE-FIRED DRY PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-006-6	Dry Process Cement Kiln	Electrostatic Precipitator	Acenaphthene	1.80E-05 (8.99E-06)	D
			Fluorene	2.77E-06 (1.39E-06)	D
			Fluoranthene	4.84E-06 (2.42E-06)	D
			Naphthalene	3.84E-04 (1.92E-04)	D
			Phenanthrene	3.37E-05 (1.69E-05)	D
			Pyrene	2.91E-06 (1.46E-06)	D
			2-Methylnaphthalene	4.11E-05 (2.06E-05)	D

[a] Kiln operating conditions: low combustion temperature; high liquid and solid hazardous waste feed.
[b] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of clinker produced.

Source: U.S. EPA, 1994.

TABLE 4.8-10. PAH EMISSION FACTORS FOR COKE/HAZARDOUS WASTE-FIRED DRY PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[b]	Emission Factor Rating
3-05-006-6	Dry Process Cement Kiln	Multicyclone/Electrostatic Precipitator	Naphthalene	1.25E-10 (6.27E-11)	D
			Phenanthrene	1.54E-11 (7.69E-12)	D

[a] Kiln operating conditions: high combustion temperature; high liquid hazardous waste feed.

[b] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of solid raw material input.

Source: U.S. EPA, 1994.

TABLE 4.8-11. PAH EMISSION FACTORS FOR COAL/HAZARDOUS WASTE-FIRED DRY PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-05-006-6	Dry Process Cement Kiln	Fabric Filter	Acenaphthene	1.88E-06 (9.40E-07)	D
			Acenaphthylene	3.99E-06 (1.99E-06)	D
			Fluorene	<1.12E-06 (<5.62E-07)	D
			Fluoranthene	2.43E-06 (1.22E-06)	D
			Naphthalene	<1.30E-04 (<6.49E-05)	D
			Phenanthrene	1.56E-05 (7.79E-06)	D
			2-Methylnaphthalene	3.60E-05 (1.80E-05)	D

[a] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of solid raw material input.

Source: U.S. EPA, 1994.

TABLE 4.8-12. PAH EMISSION FACTORS FOR COAL-FIRED PRECALCINER DRY PROCESS PORTLAND CEMENT KILNS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-05-006-6	Dry Process Cement Kiln	Fabric Filter	Benz(a)anthracene	4.3E-08 (2.1E-08)	E
			Benzo(a)pyrene	1.3E-07 (6.5E-08)	E
			Benzo(b)fluoranthene	5.6E-07 (2.8E-07)	E
			Benzo(k)fluoranthene	1.5E-07 (7.7E-08)	E
			Chrysene	1.6E-07 (8.1E-08)	E
			Dibenz(a,h)anthracene	6.3E-07 (3.1E-07)	E
			Indeno(1,2,3-cd)pyrene	8.7E-08 (4.3E-08)	E
			Acenaphthene	1.2E-04 (5.9E-05)	E
			Benzo(ghi)perylene	7.8E-08 (3.9E-08)	E
			Fluorene	1.9E-05 (9.4E-06)	E
			Fluoranthene	8.8E-06 (4.4E-06)	E
			Naphthalene	1.7E-03 (8.5E-04)	E

(continued)

TABLE 4.8-12. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-05-006-6 (continued)	Dry Process Cement Kiln (continued)	Fabric Filter (continued)	Phenanthrene	3.9E-04 (2.0E-04)	E
			Pyrene	4.4E-06 (2.2E-06)	E

[a] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of raw material input.

Source: U.S. EPA, 1994.

Source Locations

The portland cement manufacturing industry is dispersed geographically throughout the United States. Thirty-six States have at least one facility. As of December 1990, there were 119 known portland cement plants operating in the United States, operating 214 kilns with a total annual clinker capacity of 81 x 10^6 tons (73.7 x 10^6 Mg). The kiln population included 80 wet process kilns and 133 dry process kilns (U.S. EPA, 1995). Table 4.8-13 presents the number of portland cement plants and kilns in the United States by state and the associated production capacities as of December 1990.

TABLE 4.8-13. U.S. PORTLAND CEMENT PLANT LOCATIONS AND CAPACITY

Location	Number of Plants (kilns)	Capacity 10^3 tons/yr (10^3 Mg/yr)
Alabama	5 (6)	4,260 (3,873)
Alaska	1 (0)[a]	0 (0)
Arizona	2 (7)	1,770 (1,609)
Arkansas	2 (5)	1,314 (1,195)
California	12 (20)	10,392 (9,447)
Colorado	3 (5)	1,804 (1,640)
Florida	6 (8)	3,363 (3,057)
Georgia	2 (4)	1,378 (1,253)
Hawaii	1 (1)	263 (239)
Idaho	1 (2)	210 (191)
Illinois	4 (8)	2,585 (2,350)
Indiana	4 (8)	2,830 (2,573)
Iowa	4 (7)	2,806 (2,551)
Kansas	4 (11)	1,888 (1,716)
Kentucky	1 (1)	724 (658)
Maine	1 (1)	455 (414)
Maryland	3 (7)	1,860 (1,691)
Michigan	5 (9)	4,898 (4,453)
Mississippi	1 (1)	504 (458)
Missouri	5 (7)	4,677 (4,252)
Montana	2 (2)	592 (538)
Nebraska	1 (2)	961 (874)
Nevada	1 (2)	415 (377)
New Mexico	1 (2)	494 (449)
New York	4 (5)	3,097 (2,815)
Ohio	4 (5)	1,703 (1,548)

(continued)

TABLE 4.8-13. (Continued)

Location	Number of Plants (kilns)	Capacity 10^3 tons/yr (10^3 Mg/yr)
Oklahoma	3 (7)	1,887 (1,715)
Oregon	1 (1)	480 (436)
Pennsylvania	11 (24)	6,643 (6,039)
South Carolina	3 (7)	2,579 (2,345)
South Dakota	1 (3)	766 (696)
Tennessee	2 (3)	1,050 (955)
Texas	12 (20)	8,587 (7,806)
Utah	2 (3)	928 (844)
Virginia	1 (5)	1,117 (1,015)
Washington	1 (1)	473 (430)
West Virginia	1 (3)	822 (747)
Wyoming	1 (1)	461 (419)

[a] Grinding plant only.

Source: U.S. EPA, 1995.

(continued)

SECTION 4.8 REFERENCES

Behan, Frank, U.S. Environmental Protection Agency, telephone conversation with Peter Keller, Radian Corporation. "Proposed MACT Standards for BIFs." September 13, 1995.

Kim, I. "Incinerators and Cement Kilns Face Off." Chemical Engineering. April 1994.

Research Triangle Institute (RTI). Deliverable for Task 1, Work Assignment 2-39, EPA Contract 68-D2-0065. Prepared for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. 1994.

U.S. Environmental Protection Agency. Compilation of Air Pollutant Emissions Factors. Volume I: Stationary Point and Area Sources. AP-42, Fifth Edition, Section 11.6: Portland Cement Manufacturing. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. 1995.

U.S. Environmental Protection Agency. Technical Support for Revision of the Hazardous Waste Combustion Regulations for Cement Kilns and Other Thermal Treatment Devices, Second Draft. Prepared by Energy and Environmental Research Corporation for Office of Solid Waste. Work Assignment 1-10. 1994.

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. 4-1 to 4-37. December 1991.

4.9 PULP AND PAPER INDUSTRY

Chemical wood pulping involves the extraction of cellulose from wood by dissolving the lignin that binds the cellulose fibers. Kraft pulping is the major form of chemical wood pulping in the United States, accounting for approximately 85 percent of pulp production (U.S. EPA, 1993), and is expected to continue as the dominant pulping process (AWMA, 1992; Dyer et al., 1992). Semi-chemical and acid sulfite pulping constitute 6 and 4 percent of domestic pulp production, respectively (U.S. EPA, 1993).

Three combustion processes associated with the pulp and paper industry have been identified as potential sources of POM emissions: chemical recovery furnaces, lime kilns, and power boilers. Wood waste and fossil fuel-fired industrial power boiler POM emissions are discussed in Section 4.1.2 because these sources are not specific to the pulp and paper industry. The following sections focus on the pulp mill chemical recovery processes associated with potential POM emissions.

4.9.1 Kraft Recovery Furnaces

Process Description

The Kraft pulping process involves the cooking or digesting of wood chips at an elevated temperature 340 to 360°F (about 175°C) and pressure (100 to 135 psig) in white liquor, which is a water solution of sodium sulfide (Na_2S) and sodium hydroxide (NaOH). The lignin that binds the cellulose fibers is chemically dissolved by the white liquor in a tall, vertical digester. This process breaks the wood into soluble lignin and alkali-soluble hemicellulose and insoluble cellulose or pulp. A typical Kraft pulping and recovery process is shown in Figure 4.9.1-1.

Two types of digester systems are used in chemical pulping: batch and continuous. In a batch digester, the contents of the digester are transferred to an atmospheric tank, usually referred to as a blow tank, after cooking is completed (2 to 6 hours). In a

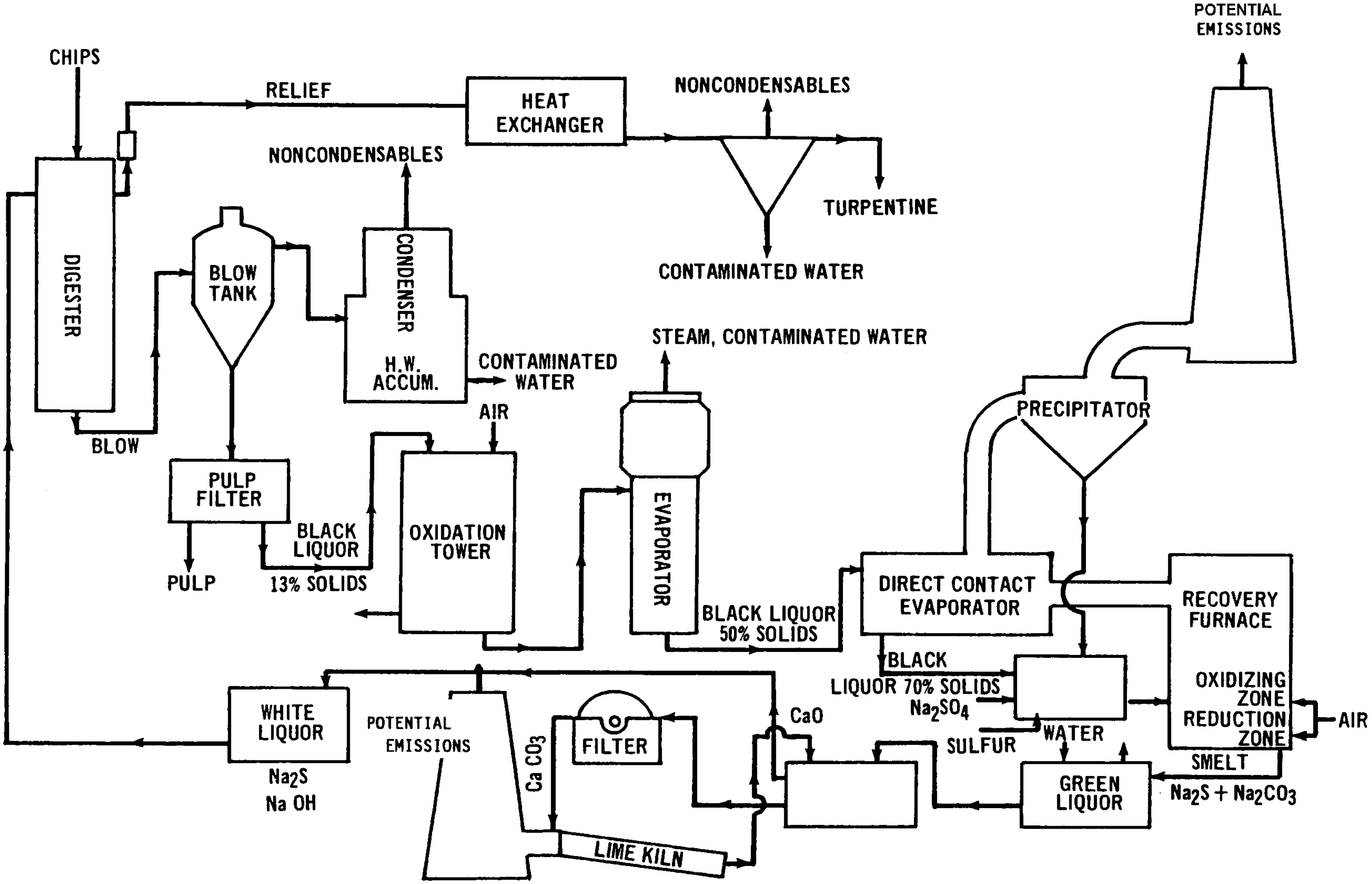


Figure 4.9.1-1. Typical Kraft Pulping and Recovery Process

Source: U.S. EPA, 1995.

POM_9411.ds4

continuous digester, wood chips and white liquor continuously enter the system from the top while pulp is continuously withdrawn from the bottom into a blow tank. In both types of digesters, the entire contents of the blow tank are diluted and pumped to a series of brown-stock washers, where the spent cooking liquor is separated from the pulp. The pulp, which may then be bleached, is pressed and dried into the finished product.

The balance of the Kraft process is designed to recover the cooking chemicals and heat. The diluted spent cooking liquor, or weak black liquor, which is 12 to 18 percent dissolved solids, is extracted from the brownstock washers and concentrated in a multiple-effect evaporator system to about 55 percent solids. The liquor is then further concentrated to 65 percent solids (strong black liquor) in a direct contact evaporator (DCE) or a nondirect contact evaporator (NDCE), depending on the configuration of the recovery furnace in which the liquor is combusted. DCE and NDCE recovery furnace schematics are shown in Figures 4.9.1-2 and 4.9.1-3, respectively.

In older recovery furnaces, the furnace's hot combustion gases concentrate the black liquor in a DCE prior to combustion. NDCEs include most furnaces built since the early 1970s and modified older furnaces that have incorporated recovery systems that eliminate the conventional DCEs. These NDCEs use a concentrator rather than a DCE to concentrate the black liquor prior to combustion. In another type of NDCE system, the multiple-effect evaporator system is extended to replace the direct contact system.

The strong black liquor is sprayed into a recovery furnace with air control to create both reducing and oxidizing zones within the furnace chamber. The combustion of the organics dissolved in the black liquor provides heat for generating process steam and, more importantly, for reducing sodium sulfate (Na_2SO_4) to Na_2S to be reused in the cooking process. Sodium sulfate, which constitutes the bulk of the particulates in the furnace flue gas, is recovered and recycled by an ESP. During combustion, most of the inorganic chemicals present in the black liquor collect as a molten smelt in the form of sodium carbonate (Na_2CO_3) and Na_2S at the bottom of the furnace, where they are continuously withdrawn into a smelt-dissolving tank.

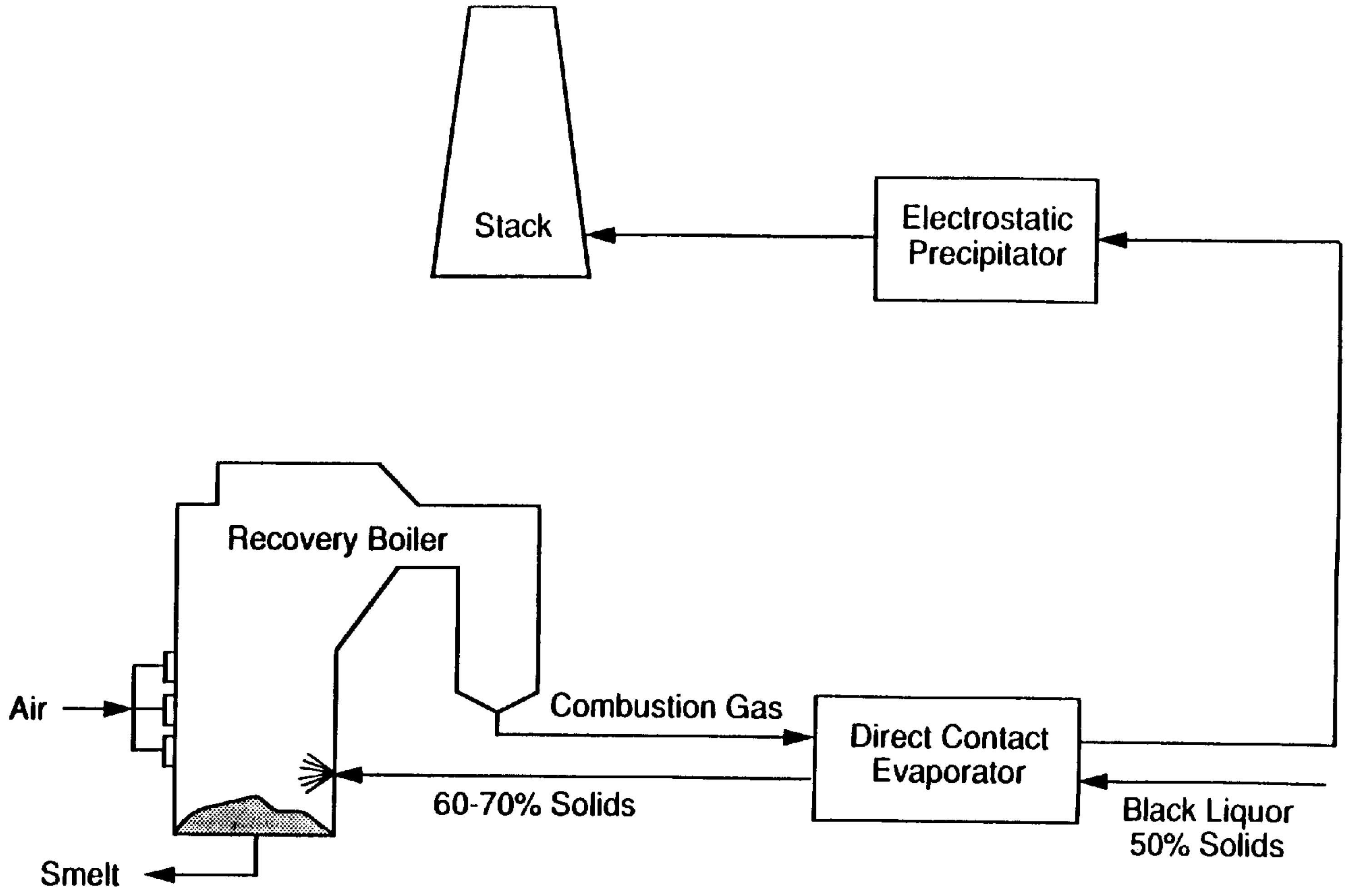


Figure 4.9.1-2. Direct Contact Evaporator Recovery Boiler

Source: Radian, 1993.

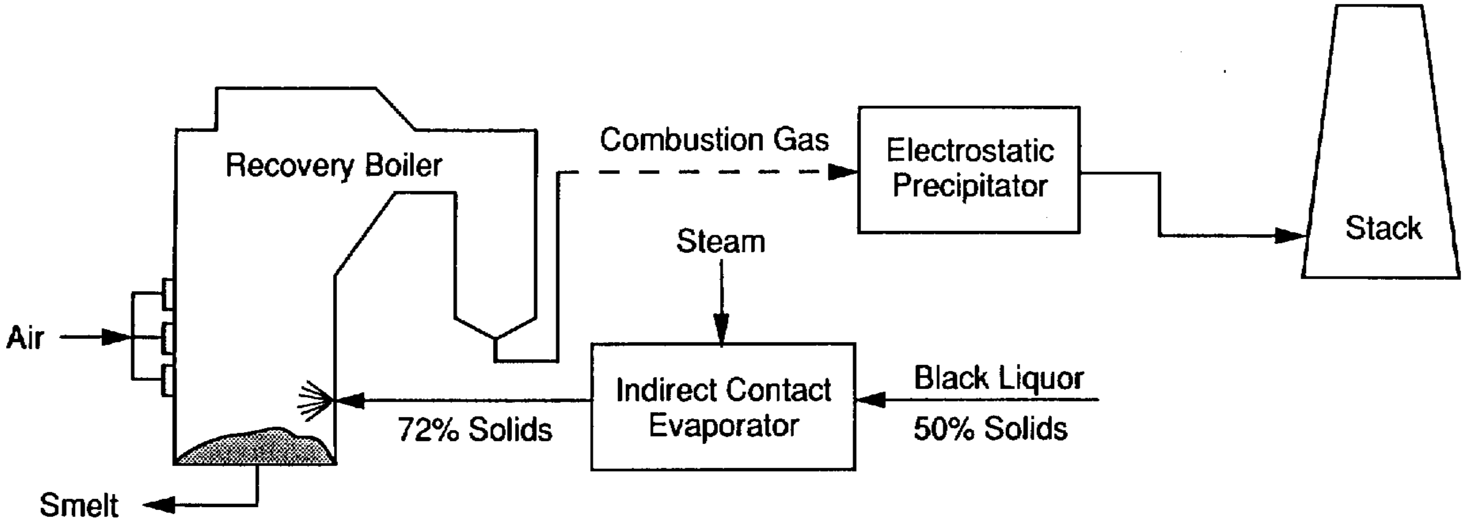


Figure 4.9.1-3. Non-direct Contact Evaporator Recovery Boiler

Source: Radian, 1993.

In addition to straight Kraft process liquor, semi-chemical pulping process spent liquor, known as brown liquor, may also be recovered in Kraft recovery furnaces. The semi-chemical pulping process is a combination of chemical and mechanical pulping processes that was developed to produce high-yield chemical pulps. In the semi-chemical process, wood chips are partially digested with cooking chemicals to weaken the bonds between the lignin and the wood. Oversize particles are removed from the softened wood chips and the chips are mechanically reduced to pulp by grinding them in a refiner. The most common type of semi-chemical pulping is referred to as neutral sulfite semi-chemical (NSSC). The only major difference between the semi-chemical process and Kraft/sulfite pulping process is that the semi-chemical digestion process is shorter and wood chips are only partially delignified. As mentioned above, some mills combine spent liquor from on-site semi-chemical processes with spent liquor from adjacent Kraft processes for cross-chemical recovery (U.S. EPA, 1993). Stand-alone, semi-chemical mills mostly recover chemicals from liquor using fluidized bed incineration or reactors, such as a Copeland reactor.

Particulate emissions from the Kraft recovery furnaces consist primarily of sodium sulfate and sodium carbonate, with some sodium chloride. Particulate control on NDCE recovery furnaces is achieved with ESPs, including both wet- and dry-bottom, and, to a lesser extent, with scrubbers. For DCEs equipped with either a cyclonic scrubber or a cascade evaporator, further particulate control is necessary because these devices are generally only 20 to 50 percent efficient for particulates (U.S. EPA, 1995). Most often in these cases, an ESP is employed after the DCE for an overall particulate control efficiency range of 85 percent to more than 99 percent. At existing mills, auxiliary scrubbers may be added to supplement older and less efficient primary particulate control devices. No specific data were available in the literature documenting POM control efficiencies for ESPs and scrubbers on Kraft black liquor recovery furnaces.

POM compound emissions from black liquor combustion are affected by furnace emission control devices as well as recovery process operating characteristics, furnace design and operation, and the characteristics of the black liquor feed. Furnace design and operation affect combustion efficiency, which is inversely related to POM emissions. The black liquor concentration process determines the percentage of organic and inorganic solids in the black liquor feed. Higher percent solids liquors which contain a greater concentration of organic compounds will exhibit better combustion properties due to the higher heating value of the liquor.

Emission Factors

Emission factors for PAHs from three Kraft recovery furnace/control configurations were reported by the National Council for Air and Stream Improvement, an industry environmental research organization (NCASI, 1993). The three furnace/control configurations represented included a DCE recovery furnace equipped with a wet-bottom ESP and scrubber in series, an NDCE recovery furnace equipped with a dry-bottom ESP, and an NDCE recovery furnace equipped with a dry-bottom ESP and wet scrubber in series. Sampling was conducted for 16 PAHs using CARB Method 429. The resultant controlled emission factors represent both vapor-phase and particulate PAHs and are expressed in units of pound of PAH per air dry ton of pulp produced (lb/ADTP) and kilogram of PAH per air dry metric ton of pulp produced (kg/ADMT). The black liquor solids (BLS) fired in a Kraft recovery boiler can be correlated to ADTP by a factor of approximately 3,000 lb of BLS per ADTP (NCASI, 1993). PAH emission factors for Kraft black liquor recovery furnaces are presented in Table 4.9.1-1.

Source Locations

The distribution of Kraft pulp mills in the United States in 1993 is shown in Table 4.9.1-2. Kraft pulp mills are located primarily in the southeast, whose forests provide over 60 percent of U.S. pulpwood.

TABLE 4.9.1-1. PAH EMISSION FACTORS FOR KRAFT PROCESS RECOVERY FURNACES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ADTP (kg/ADMT)[a]	Emission Factor Range in lb/ADTP (kg/ADMT)[a]	Emission Factor Rating
3-07-001-04	Nondirect-Contact Evaporator Kraft Recovery Furnace	Dry-Bottom ESP	Benz(a)anthracene	<1.20E-05 (<6.00E-06)	---	D
			Benzo(a)pyrene	<2.60E-06 (<1.30E-06)	---	D
			Benzo(b)fluoranthene	<6.40E-06 (<3.20E-06)	---	D
			Chrysene	5.50E-05 (2.75E-05)	---	D
			Dibenz(a,h)anthracene	<6.00E-06 (<3.00E-06)	---	D
			Indeno(1,2,3-cd)pyrene	<6.00E-06 (<3.00E-06)	---	D
			Acenaphthene	<5.00E-06 (<2.50E-06)	---	D
			Benzo(ghi)perylene	7.90E-06 (3.59E-06)	---	D
			Pyrene	1.00E-04 (5.00E-05)	---	D
3-07-001-04	Direct-Contact Evaporator Kraft Recovery Furnace	Wet-Bottom ESP	Naphthalene	5.95E-03 (2.98E-03)	3.3E-3 - 8.6E-3 (1.7E-3 - 4.3E-3)	D
3-07-001-04	Direct-Contact Evaporator Kraft Recovery Furnace	Wet-Bottom ESP/Scrubber	Benz(a)anthracene	9.60E-05 (4.80E-05)	---	D
			Benzo(a)pyrene	5.80E-06 (2.90E-06)	---	D

(continued)

TABLE 4.9.1-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ADTP (kg/ADMT)[a]	Emission Factor Range in lb/ADTP (kg/ADMT)[a]	Emission Factor Rating
3-07-001-04 (continued)	Direct-Contact Evaporator Kraft Recovery Furnace (continued)	Wet-Bottom ESP/Scrubber (continued)	Benzo(b)fluoranthene	2.90E-05 (1.45E-05)	---	D
			Benzo(k)fluoranthene	8.00E-06 (4.00E-06)	---	D
			Chrysene	3.90E-05 (1.95E-05)	---	D
			Dibenz(a,h)anthracene	6.80E-06 (3.40E-06)	---	D
			Indeno(1,2,3-cd)pyrene	4.20E-06 (2.10E-06)	---	D
			Acenaphthene	1.60E-05 (8.00E-06)	---	D
			Acenaphthylene	2.60E-03 (1.30E-03)	---	D
			Anthracene	4.00E-04 (2.00E-04)	---	D
			Benzo(ghi)perylene	1.20E-05 (6.00E-06)	---	D
			Fluoranthene	6.90E-04 (3.45E-04)	---	D
			Fluorene	2.10E-04 (1.05E-04)	---	D
			Naphthalene	3.20E-02 (1.60E-02)	---	D

(continued)

TABLE 4.9.1-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ADTP (kg/ADMT)[a]	Emission Factor Range in lb/ADTP (kg/ADMT)[a]	Emission Factor Rating
3-07-001-04 (continued)	Direct-Contact Evaporator Kraft Recovery Furnace (continued)	Wet-Bottom ESP/Scrubber (continued)	Phenanthrene	5.60E-03 (2.80E-03)	---	D
			Pyrene	3.30E-04 (1.65E-04)	---	D
3-07-001-10	Indirect-Contact Evaporator Kraft Recovery Furnace	Dry-Bottom ESP/Scrubber	Naphthalene	8.70E-04 (4.35E-04)	---	D
			Benz(a)anthracene	<3.50E-06 (<1.75E-06)	---	D
			Benzo(a)pyrene	<3.50E-06 (<1.75E-06)	---	D
			Benzo(b)fluoranthene	<3.50E-06 (<1.75E-06)	---	D
			Benzo(k)fluoranthene	<3.50E-06 (<1.75E-06)	---	D
			Chrysene	<3.50E-06 (<1.75E-06)	---	D
			Dibenz(a,h)anthracene	<3.50E-06 (1.75E-06)	---	D
			Indeno(1,2,3-cd)pyrene	<3.50E-06 (<1.75E-06)	---	D
			Acenaphthene	<3.50E-06 (<1.75E-06)	---	D
			Acenaphthylene	1.30E-05 (6.50E-06)	---	D

(continued)

TABLE 4.9.1-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ADTP (kg/ADMT)[a]	Emission Factor Range in lb/ADTP (kg/ADMT)[a]	Emission Factor Rating
3-07-001-10 (continued)	Indirect-Contact Evaporator Kraft Recovery Furnace (continued)	Wet-Bottom ESP/Scrubber (continued)	Anthracene	<3.50E-06 (<1.75E-06)	---	D
			Benzo(ghi)perylene	<3.50E-06 (<1.75E-06)	---	D
			Fluoranthene	1.90E-05 (9.50E-06)	---	D
			Fluorene	<3.50E-06 (<1.75E-06)	---	D
			Phenanthrene	9.50E-05 (4.75E-05)	---	D
			Pyrene	1.10E-05 (5.50E-06)	---	D

[a] Emission factors are in lb (kg) of pollutant emitted per ADTP (ADMT) of pulp produced.

Source: NCASI, 1993.

TABLE 4.9.1-2. DISTRIBUTION OF KRAFT PULP MILLS IN THE UNITED STATES (1993)

State	Number of Mills
Alabama	16
Arizona	2
Arkansas	7
California	3
Florida	11
Georgia	13
Idaho	1
Kentucky	2
Louisiana	11
Maine	8
Maryland	1
Michigan	3
Minnesota	3
Mississippi	5
Montana	2
New Hampshire	2
New York	1
North Carolina	7
Ohio	1
Oklahoma	1
Oregon	7
Pennsylvania	4
South Carolina	6

(continued)

TABLE 4.9.1-2. (Continued)

State	Number of Mills
Tennessee	3
Texas	8
Virginia	5
Washington	12
Wisconsin	4
Total	149

Source: U.S. EPA, 1993.

4.9.2 Lime Kilns

Process Description

In the Kraft pulping process, molten smelt leaving the recovery furnace is contacted with mill water or weak wash in the smelt dissolving tank to form green liquor. Weak wash is the filtrate from lime mud washing. The green liquor is clarified and reacted with burnt lime (CaO) in a lime slaker. Following a series of causticizing vessels, the resultant white liquor is clarified to yield Na_2S + NaOH (aqueous white liquor) and lime mud or calcium carbonate ($CaCO_3$). The white liquor is recycled to the digestion process and the lime mud is calcined in a lime kiln to regenerate CaO (Radian, 1993).

A lime kiln is a countercurrent, inclined tube process heater designed to convert lime mud ($CaCO_3$) to CaO for reuse in the causticizing of Kraft liquor. A process flow diagram for a lime kiln is shown in Figure 4.9.2-1. The rotary kiln is the most common lime kiln design used in the Kraft pulp and paper industry. Rotary lime kilns range from 8 to 13 feet (2.4 to 4.0 m) in diameter, and from 100 to 400 feet (30 to 120 m) in length. Lime kilns predominantly fire natural gas, with some units firing distillate and/or residual fuel oil. Many facilities incinerate non-condensible gases (NCG) from pulping source vents in lime kilns to control total reduced sulfur (TRS) emissions. Temperatures in the kiln can range from 300 to 500°F (150 to 260°C) at the upper or wet end to 2,200 to 2,400°F (1,200 1,300°C) at the hottest part of the calcination zone near the lower or dry end (U.S. EPA, 1976; Radian, 1993).

Emissions of concern from lime kilns include PM, largely in the form of calcium salts, SO_2, NO_x, and organics from either water evaporated from the lime mud in the kiln or the scrubbing medium employed. Emissions of POM from lime kilns are likely due almost entirely to the combustion of fossil fuel (natural gas or fuel oil). The most common control technologies used on lime kilns are scrubbers, although some ESPs are also used. Scrubbers are used on lime kilns primarily for control of particulate emissions. These scrubbers use either fresh water or clean condensates from pulping sources as scrubbing solutions. Small amounts of caustic solution may be added to the scrubber solution to scrub TRS and SO_2. Lime kiln scrubber

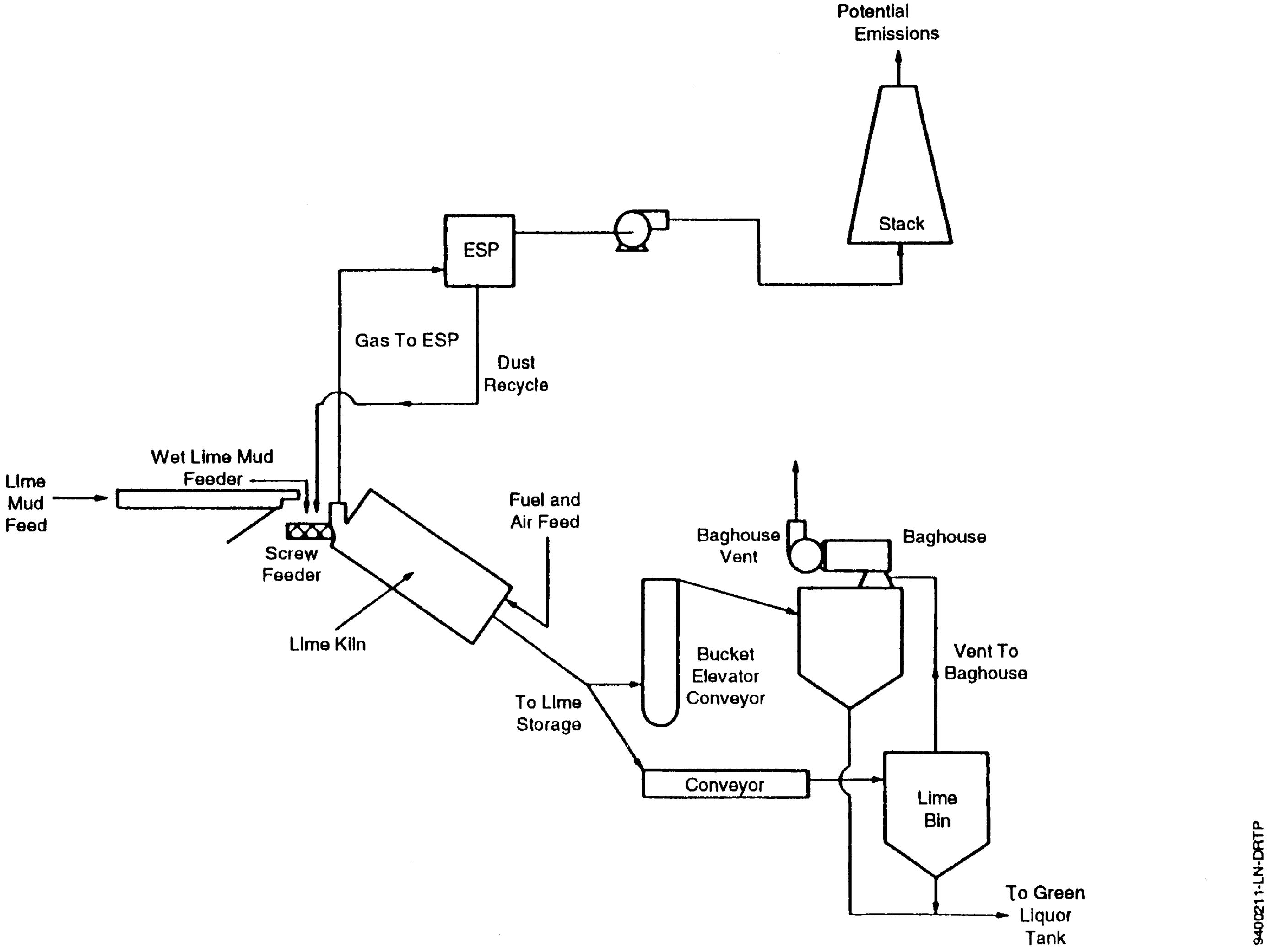


Figure 4.9.2-1. Process Flow Diagram for a Lime Kiln

Source: Radian, 1993.

designs include impingement, venturi, and cyclonic scrubbers. Scrubbers and ESPs can provide control of particulate POM emissions. Additionally, wet scrubbers may provide some control of vapor-phase POM by condensation and solution in the scrubbing medium (NCASI, 1993).

Emission Factors

PAH emission factors for two scrubber-controlled lime kilns under four fuel firing scenarios are presented in Table 4.9.2-1. The scenarios include natural gas, natural gas/coke, natural gas/NCG, and natural gas/tire-derived fuel (TDF). The data reported by NCASI (1993) were based on sampling and analysis for naphthalene only. The sampling methods used were CARB Method 429 and EPA Reference Method 18. The emission factors reported by EPA (1991) were based on an unspecified sampling protocol that was assumed to conform with EPA-approved methodology.

Source Locations

Lime kilns are located at Kraft process pulp mills. See Table 4.9.1-2 Section 4.9.1 for Kraft pulp mill source locations reported in 1993.

4.9.3 Sulfite Recovery Furnaces

Process Description

Although not as commonplace, the acid sulfite pulp production process is similar to the Kraft process except that different chemicals are used for cooking. Sulfurous acid is used in place of a caustic solution to dissolve wood lignin. To buffer the cooking solution, a bisulfite of sodium, magnesium, calcium, or ammonium is used. Digestion occurs under high temperature and pressure, as in the Kraft process, in either batch mode or continuous digesters. Following digestion and discharge of the pulp into an atmospheric blow pit or dump tank, the spent sulfite liquor, known as red liquor, may be treated and discarded, incinerated, or sent through a recovery

TABLE 4.9.2-1. PAH EMISSION FACTORS FOR PULP MILL LIME KILNS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ)[a]	Emission Factor Rating	Reference
3-07-001-06	Gas-Fired Lime Kiln	Scrubber	Benz(a)anthracene	1.10E-06 (4.73E-07)	D	U.S. EPA, 1991
			Benzo(b)fluoranthene	8.00E-07 (3.44E-07)	D	U.S. EPA, 1991
			Benzo(k)fluoranthene	3.00E-07 (1.29E-07)	D	U.S. EPA, 1991
			Chrysene	1.10E-06 (4.73-07)	D	U.S. EPA, 1991
			Anthracene	3.70E-06 (1.59E-06)	D	U.S. EPA, 1991
			Fluoranthene	8.60E-06 (3.70E-06)	D	U.S. EPA, 1991
			Naphthalene	0.036 (0.018)[b]	D	NCASI, 1993
			Phenanthrene	5.19E-05 (2.23E-05)	D	U.S. EPA, 1991
			Pyrene	6.60E-06 (2.84E-06)	D	U.S. EPA, 1991
3-07-001-06	Gas-/TDF-Fired Lime Kiln[c]	Scrubber	Benz(a)anthracene	1.10E-06 (4.73E-07)	D	U.S. EPA, 1991
			Benzo(b)fluoranthene	8.00E-07 (3.44E-07)	D	U.S. EPA, 1991
			Benzo(k)fluoranthene	4.00E-07 (1.72E-07)	D	U.S. EPA, 1991
			Chrysene	1.10E-06 (4.73E-07)	D	U.S. EPA, 1991

(continued)

TABLE 4.9.2-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/MMBtu (g/MJ)[a]	Emission Factor Rating	Reference
3-07-001-06 (continued)	Gas-/TDF-Fired Lime Kiln[c] (continued)	Scrubber (continued)	Anthracene	1.80E-06 (7.74E-07)	D	U.S. EPA, 1991
			Fluoranthene	8.80E-06 (3.78E-06)	D	U.S. EPA, 1991
			Phenanthrene	2.91E-05 (1.25E-05)	D	U.S. EPA, 1991
			Pyrene	6.20E-06 (2.67E-06)	D	NCASI, 1993
3-07-001-06	Gas-Fired Lime Kiln Burning NCG[d]	Scrubber	Naphthalene	6.50E-03 (3.25E-03)[b]	D	NCASI, 1993
3-07-001-06	Gas-/Coke-Fired Lime Kiln	Scrubber	Naphthalene	4.60E-03 (2.30E-03)[b]	D	NCASI, 1993

[a] Emission factors are in lb (g) of pollutant emitted per MMBtu (MJ) of heat input, except as noted.
[b] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of calcium oxide produced.
[c] Lime kiln firing 85 percent natural gas and 15 percent TDF.
[d] NCD from pulping and chemical recovery operations are incinerated in the lime kiln to reduce total reduced sulfur (TRS) emissions to the atmosphere.

process for recovery of heat and chemicals. Additionally, chemicals can be recovered from gaseous streams such as those from red stock washers. The cost of the soluble bases, with the exception of calcium, makes chemical recovery economically feasible (U.S. EPA, 1995; U.S. EPA, 1993). A simplified process schematic of magnesium-base sulfite pulping and chemical recovery is shown in Figure 4.9.3-1.

Emission Factors

Only one PAH emission factor was available in the literature for naphthalene from an uncontrolled ammonia-base sulfite recovery furnace. The naphthalene emission factor is presented in Table 4.9.3-1.

Source Locations

Sulfite recovery furnaces are located at sulfite process pulp mills. Table 4.9.3-2 shows the distribution of sulfite pulp mills in the United States in 1993 according to information compiled in support of EPA's pulp and paper industry MACT standard development.

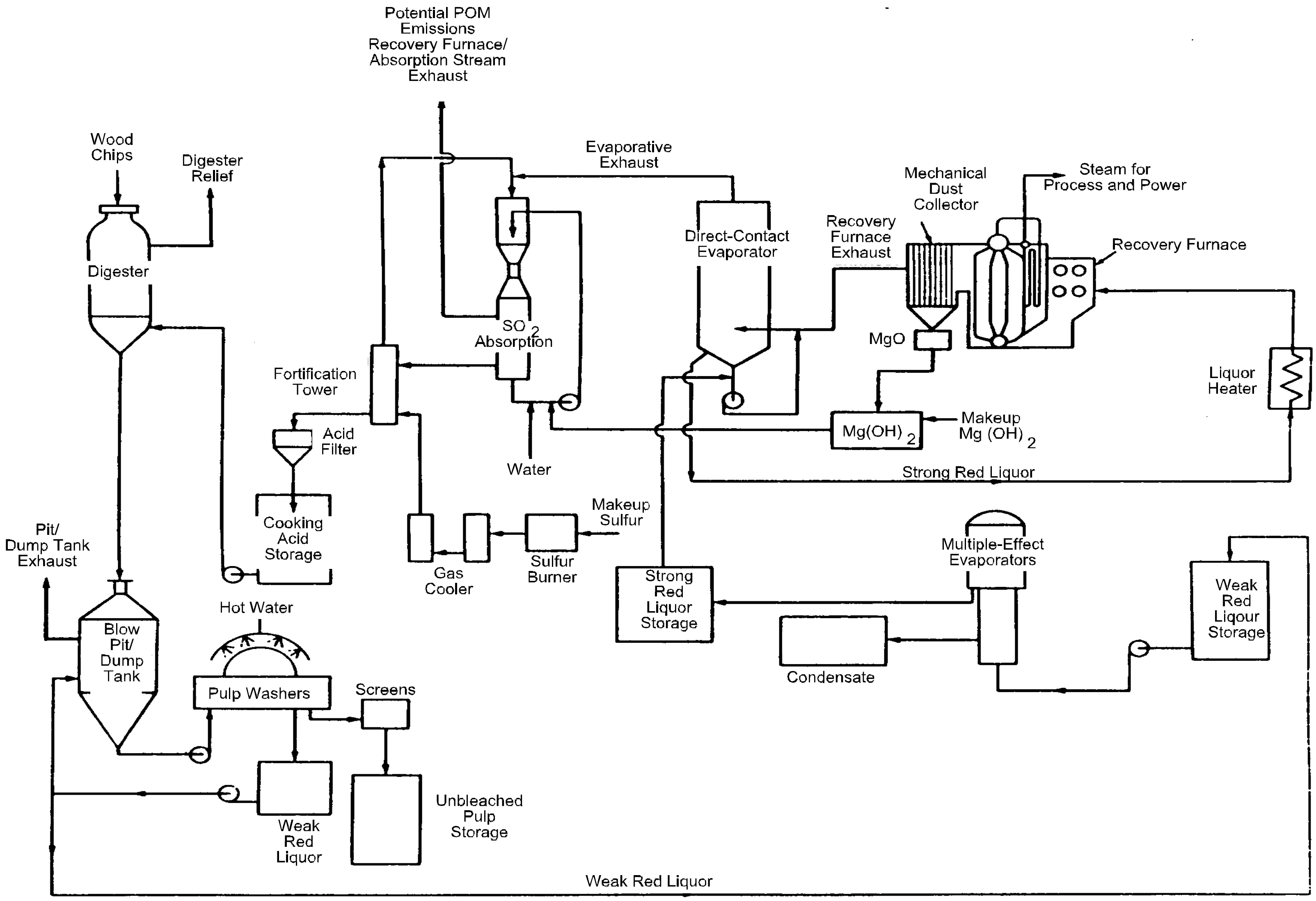


Figure 4.9.3-1. Process Diagram for Magnesium-Based Sulfite Pulping and Chemical Recovery

Source: U.S. EPA, 1995.

TABLE 4.9.3-1. PAH EMISSION FACTORS FOR SULFITE PROCESS RECOVERY FURNACES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ADTP (kg/ADMT)[a]	Emission Factor Rating
3-07-002-22	Ammonia-Based Sulfite Recovery Furnace	None	Naphthalene	4.30E-03 (2.15E-03)	D

[a] Emission factor is in lb (kg) of naphthalene emitted per ADTP (ADMT) of pulp produced.

Source: NCASI, 1993.

TABLE 4.9.3-2. DISTRIBUTION OF SULFITE PULP MILLS IN THE UNITED STATES (1993)

State	Number of Mills
Alaska	2
Florida	1
Maine	1
New York	1
Pennsylvania	1
Washington	5
Wisconsin	5
Total	16

Source: U.S. EPA, 1993.

SECTION 4.9 REFERENCES

Air and Waste Management Association (AWMA). Air Pollution Engineering Manual. Chapter 18, “Wood Processing Industry.” Van Nostrand Reinhold, New York. 1992.

Dyer, H., S. Gajita, and M. Fennessey. 1992 Lockwood-Post’s Directory of the Pulp, Paper and Allied Trades. Miller Freeman Publications, San Francisco, California. 1992.

National Council of the Paper Industry for Air and Stream Improvement (NCASI). “Compilation of Air Toxic Emission Data for Boilers, Pulp Mills, and Bleach Plants.” NCASI Inc., 260 Madison Avenue, New York, New York. Technical Bulletin No. 650, pp. 1-17 and 71-106. June 1993.

Radian Corporation. “Pulp and Paper Industry Training Session Notes.” 1993.

U.S. Environmental Protection Agency. Compilation of Air Pollution Emission Factors - AP-42 Section 10.2: Chemical Wood Pulping. Fifth Edition. Research Triangle Park, North Carolina. 1995.

U.S. Environmental Protection Agency. Pulp, Paper, and Paperboard Industry -Background Information for Proposed Air Emission Standards: Manufacturing Processes at Kraft, Sulfite, Soda, and Semi-Chemical Mills. Emission Standards Division, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-453/R-93-050a. pp. 2-1 to 2-22. 1993.

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. 4-1 to 4-37. 1991.

U.S. Environmental Protection Agency. Environmental Pollution Control - Pulp and Paper Industry, Part 1: Air. Emission Standards Division, Research Triangle Park, North Carolina. EPA-625/7-76-001. pp. 11-1 to 11-11. October 1976.

U.S. Environmental Protection Agency. Pulp, Paper, and Paperboard Industry -Background Information for Promulgated Air Emission Standards: Manufacturing Processes at Kraft, Sulfite, Soda, Semi-Chemical Mills, Mechanical, and Secondary and Non-wood Fiber Mills. Emission Standards Division, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-453/R-93-050b. p. 20-5. 1997.

4.10 OPEN BURNING

Open burning, for the purposes of this document, includes wildfires, prescribed burning (including agricultural burning and burning associated with forest management), burning of landscaping refuse, coal refuse burning, and controlled open burning of tires and plastic. The activity associated with each of these source categories can vary greatly from year to year depending on natural conditions, as in the case of wildfires, or on user practices. All of these sources, however, have been associated with POM emissions through laboratory or field emissions tests. The main source of emissions is the combustion of the particular fuel material (i.e., the live vegetation or dead organic material).

4.10.1 Wildfires and Prescribed Burning

Process Description

Wildfires refer to uncontrolled forest fires, whereas prescribed burning involves the operation and management of a controlled burn of timber or agricultural vegetation and debris. The basic process in both that results in POM emissions is very similar. Both of these sources often involve incomplete combustion of the fuel (i.e., the wood, leaves, etc.) due to the high moisture content, of the fuel varying composition of the fuel, and the limited control of the combustion process.

The most important fuel characteristics affecting emissions from wildfires and prescribed burning are fuel moisture content and fuel loading (i.e., amount of fuel per unit area). Fuel arrangement and fuel species composition (i.e., fuel type, fuel age, and fuel size) are also key variables affecting emissions. High moisture content reduces combustion efficiency, which in turn produces greater emissions. Fuel loading level is directly related to emissions, the more fuel burned, the greater the emissions. Fuel arrangement can affect burn intensity and completeness by affecting air supply and may influence the fire spreading pattern.

Fuel composition affects emissions in several ways. Different fuels (wood, grass, brush, leaves) have varying compositions, which upon combustion, produce different qualities and quantities of emissions. Fuels of differing ages contain varying moisture contents (seasoned versus green fuels) and varying organic constituents which may affect overall burning emissions. Emissions may also be affected if fuel composition has been modified by organic forest treatment chemicals such as pesticides, herbicides, etc. (Chi et al., 1979; McMahon and Tsoukalas, 1978).

Following is a brief description of wildfires and prescribed burning and their main emission characteristics.

Wildfires--Wildfires naturally occur from lightning strikes or can be accidently or intentionally started by humans. These fires tend to spread unpredictably and are often times out of control. Emissions from uncontrolled forest fires are affected primarily by environmental factors and fuel conditions. The most prominent environmental factors influencing emissions are wind speed and direction, rainfall history, and relative humidity. Secondary environmental factors include degree of cloud cover, air temperature, atmospheric stability, and degree of land slope. Wind speed, wind direction, and, to a lesser extent, slope of land all determine how fast a wildfire will spread. Generally, a faster moving fire front burns less efficiently, producing more smoldering and greater emissions (Chi et al., 1979).

Prescribed Burning--For this report prescribed burning is defined as the application and confinement of fire under specified conditions of weather, fuel moisture and soil moisture in a forest, or range, or for agricultural land management. Prescribed burning should accomplish planned benefits such as fire hazard reduction, control of understory species, seedbed and site preparation, grazing enhancement, wildlife habitat improvement, or forest tree disease control. It differs from uncontrolled wildfires in that it is used only under controlled conditions and is managed so that beneficial effects outweigh possible detrimental impacts.

Agricultural burning involves the purposeful combustion of field crop, row crop, and fruit and nut crop residues to achieve one or a combination of desired objectives. The typical objectives of agricultural burning are as follows (Kelly, 1983; Chi and Zanders, 1977).

- Removal and disposal of agricultural residue at a low cost;
- Preparation of farmlands for cultivation;
- Cleaning of vines and leaves from fields to facilitate harvest operations;
- Disease control;
- Direct weed control by incinerating weed plants and weed seeds;
- Indirect weed control by providing clean soil surface for soil-active herbicides; and
- Selective destruction of mites, insects, and rodents.

The types of agricultural waste subject to burning include residues such as rice straw and stubble; barley straw and stubble; wheat residues; prunings and natural attrition losses in orchards; grass straw and stubble; potato and peanut vines; tobacco stalks; soybean residues; hay residues; sugarcane leaves and tops; and farmland grass and weeds.

Polycyclic organic matter is created and emitted during agricultural burning due to POM mixing between the fuel (agricultural residue) and ambient air, and because combustion gases are effectively quenched by surrounding ambient air. Poor mixing creates pyrolytic (oxygen deficient) combustion conditions leading to lower temperatures, less efficient combustion, and POM formation and release. Rapid quenching of combustion gases by the huge volumes of air surrounding agricultural burning enhances incomplete combustion, thereby permitting the increased release of unburned hydrocarbons like POM. Polycyclic organic matter may be released from agricultural burning in gaseous form or as a liquid aerosol condensed on solid particulate matter (Kelly, 1983; Chi and Zanders, 1977).

When prescribed burning is used, emissions control and/or emissions impact reduction can be effected by utilizing low emission fuel conditions, firing techniques, and meteorological conditions. Fuel conditions can be optimized and overall POM emissions reduced by:

- Regulating the time between burns to control fuel loading;
- Burning at lower fuel moisture contents; and
- Modifying fuel arrangement to facilitate better air flow and more intense and complete combustion.

The firing techniques involved in forest management and agricultural burning can vary widely depending on the specific plant species, the local climate, and any applicable regulations that may be in effect.

Emission Factors

Limited amounts of POM emission factor data were found that are based on tests of actual prescribed burning or uncontrolled forest fires. However, emission factor data have been developed by the U.S. Forest Service by simulating forest burning conditions in a laboratory. In one test, various loadings of pine needles were burned on a metal table equipped to change slope to simulate wind effects (McMahon and Tsoukalas, 1978). All emissions from burning were channeled through a large stack where particulate matter was collected on a glass fiber filter in a modified high-volume sampler. Collected samples were analyzed for POM compounds by GC/MS. The results of these tests are given in Table 4.10.1-1.

The PAH emission factors that are based on the study by McMahon and Tsoukalas are presented in Table 4.10.1-1 and represent the average emissions during the flaming and smoldering phases of a fire. The factors could conceivably be used for either estimating emissions from wildfires or prescribed burning of pine trees material. These factors should not be considered to be representative of burning in hardwood forests or areas where the vegetation is more varied.

Table 4.10.1-1 also presents a set of PAH emission factors that represent both wildfires and prescribed burning (forest and agricultural), with no specific vegetation type identified (Versar Inc., 1989). These factors are also based on laboratory testing conditions, and

TABLE 4.10.1-1. PAH EMISSION FACTORS FOR WILDFIRES AND PRESCRIBED BURNING

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/kg)[a]	Emission Factor Rating	Reference
A28-10-001-000/ A28-10-010-000	Forest Wildfires/ Slash, Prescribed Burning (from the burning of pine needles)	None	Benzo(a)pyrene	1.48E-03 (0.74)	E	McMahon and Tsoukalas, 1978
			Benzofluoranthenes	5.14E-03 (2.57)	E	McMahon and Tsoukalas, 1978
			Chrysene/Benz(a)anthracene	1.27E-02 (6.32)	E	McMahon and Tsoukalas, 1978
			Indeno(1,2,3-cd)pyrene	3.41E-03 (1.70)	E	McMahon and Tsoukalas, 1978
			Benzo(ghi)perylene	5.08E-03 (2.54)	E	McMahon and Tsoukalas, 1978
			Anthracene/Phenanthrene	9.95E-03 (4.96)	E	McMahon and Tsoukalas, 1978
			Fluoranthene	6.73E-03 (3.36)	E	McMahon and Tsoukalas, 1978
			Pyrene	9.29E-03 (4.64)	E	McMahon and Tsoukalas, 1978
			Benzo(e)pyrene	2.66E-03 (1.33)	E	McMahon and Tsoukalas, 1978
			Methylanthracene	8.23E-03 (4.10)	E	McMahon and Tsoukalas, 1978
			Perylene	8.56E-04 (0.43)	E	McMahon and Tsoukalas, 1978
			Benzo(c)phenanthrene	3.90E-03 (1.95)	E	McMahon and Tsoukalas, 1978

(continued)

TABLE 4.10.1-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/kg)[a]	Emission Factor Rating	Reference
A28-10-001-000/ A28-10-010-000 (continued)	Forest Wildfires/Slash, Prescribed Burning (from the burning of pine needles) (continued)	None	Methylbenzopyrenes	2.96E-03 (1.48)	E	McMahon and Tsoukalas, 1978
			Methylchrysene	7.90E-03 (3.94)	E	McMahon and Tsoukalas, 1978
			Methylpyrene, -fluoranthene	9.05E-03 (4.52)	E	McMahon and Tsoukalas, 1978
A28-10-001-000/ A28-10-010-000/ A28-01-500-000	Forest Wildfires/Slash, Prescribed Burning/ Agricultural Burning (exact source unspecified)	None	Benz(a)anthracene	6.20E-03 (3.09)	U	Versar, Inc., 1989
			Benzo(a)pyrene	1.50E-03 (0.75)	U	Versar, Inc., 1989
			Benzo(k)fluoranthene	2.60E-03 (1.30)	U	Versar, Inc., 1989
			Chrysene	6.20E-03 (3.09)	U	Versar, Inc., 1989
			Indeno(1,2,3-cd)pyrene	2.40E-03 (1.20)	U	Versar, Inc., 1989
			Benzo(ghi)perylene	5.00E-03 (2.49)	U	Versar, Inc., 1989
			Anthracene	5.00E-03 (2.49)	U	Versar, Inc., 1989
			Fluoranthene	1.10E-02 (5.49)	U	Versar, Inc., 1989

(continued)

TABLE 4.10.1-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/kg)[a]	Emission Factor Rating	Reference
A28-10-001-000/ A28-10-010-000/ A28-01-500-000 (continued)	Forest Wildfires/Slash, Prescribed Burning/ Agricultural Burning (exact source unspecified) (continued)	None	Phenanthrene	5.00E-03 (2.49)	U	Versar, Inc., 1989
			Pyrene	9.20E-03 (4.59)	U	Versar, Inc., 1989
			Benzo(a)fluoranthene	2.60E-03 (1.30)	U	Versar, Inc., 1989
A28-10-010-000	Slash, Prescribed Burning (Temperate and Boreal Forest)	None	Benzo(a)pyrene	4.49E-04 (0.22)	D	Ward and Hao, 1992
A28-01-500-000	Burning Sugar Cane (Whole Cane and Leaf Trash)	None	Benzo(a)pyrene	4.75E-04 (0.24)	E	Chi and Zanders, 1977

[a] Emission factors are expressed in lb (mg) of pollutant per ton (kg) of fuel (wood, brush, vegetation, etc.) burned.

therefore will not necessarily represent the wide range of combustion conditions that would be experienced in the field.

The factor listed for benzo(a)pyrene for slash/prescribed burning, which is based on the Ward and Hao, 1992 document, was developed from actual field test data in combination with laboratory research. The field tests were conducted in forest areas in the States of Washington and Oregon. A total of 38 fires were studied, involving a variety of fuel types and burning conditions. The benzo(a)pyrene factor listed is representative of temperate forests that would typically be found in many areas of the United States.

Few POM emission factors exist that are specific to agricultural burning. The factors that are available pertain only to benzo(a)pyrene. Burning of whole sugar cane residue and sugar cane leaf trash were found to produce particulate emissions of benzo(a)pyrene (Chi and Zanders, 1977). Agricultural burning has received significant attention due to the proximity of burning to human population areas.

Source Locations

Information provided by the U.S. Forest Service indicates that the majority of prescribed burning in the United States occurs in the southern/southeastern part of the country (Cruse, 1986). Sixty percent of national prescribed burning in 1984 was performed in the southern/southeastern region. The second most prevalent source of prescribed burning in 1984 was the Pacific Northwest which constituted almost 20 percent of the total; California contributed 10 percent of the national total (U.S. Forest Service, 1986).

Peterson and Ward, compiled an estimate of the area burned by prescription in 1989 for the entire United States. The total area burned for the United States was over 4.9 million acres (2 million hectares). The authors estimated that the number of hectares burned nationally during 1989 that were reported in their study may have been underestimated by a half a million hectares (Peterson and Ward, 1989).

Peterson and Ward also estimated the amount of acreage burned in different regions of the country. Their findings agreed with the conclusions of the U.S. Forest Service that are presented above; namely, that the majority (71 percent) of prescribed burning occurs in the southern/southeastern part of the United States. The states identified being in the southern/southeastern part of the United States include Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, and Tennessee.

The locations of uncontrolled forest fires are not as definable as prescribed burning sites, but the historical record of fires and a knowledge of the locations of primary forest resources can be used to estimate where the majority of forest fires are likely to occur. The southern region and the western part of the country (including California, the Pacific northwest, and western mountain states) appear to represent the greatest potential for POM emissions from forest wildfires (Siebert et al., 1978). Forest Service data for 1983 indicate that the southern/southeastern region of the United States constituted 67 percent of the total number of acres burned by wildfires nationally. The western regions of the country contained 17 percent of the wildfire burned acreage. The northern region (Idaho, Montana, North Dakota) of the country contained another 6 percent of acreage destroyed by wildfires (U.S. Forest Service, 1986).

Agricultural burning is directly correlated significant agriculture industry. Major agricultural states comprising the majority of agricultural burning include California, Louisiana, Florida, Hawaii, North Carolina, Mississippi, and Kansas (Kelly, 1983).

SECTION 4.10.1 REFERENCES

Chi, C.T. et al. Source Assessment: Prescribed Burning, State of the Art. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. EPA Report No. 600/2-79-019h. November 1979.

Chi, C.T., and D.L. Zanders. Source Assessment: Agricultural Open Burning, State of the Art. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. EPA Report No. 600/2-77-107a. July 1977.

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. 5-3 to 5-9. 1983.

McMahon, C.K., and S.N. Tsoukalas. “Polynuclear Aromatic Hydrocarbons in Forest Fire Smoke.” In: Polynuclear Aromatic Hydrocarbons: Analysis, Chemistry, and Biology, Proceedings of the Second International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1977. P.W. Jones and R.I. Freudenthal, eds. Raven Press, New York. pp. 61-73. 1978.

Peterson, J., and D. Ward. An Inventory of Particulate Matter and Air Toxics Emissions from Prescribed Fires in the United States for 1989. Pacific Northwest Research Station, Seattle, Washington. Final Report. USDA Forest Service Technical Report AG No. DW12934736-01-0-1989. 1992.

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, Pollutant Strategies Branch, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. Prepared under EPA Contract No. 68-02-2836. pp. 99-102. November 1978.

U.S. Forest Service. Information submitted to Cruse, P.A., Radian Corporation by Hansen, K., Forest Service Reports on Wildfire Statistics for 1978 to 1983. June 23, 1986.

Versar, Inc. Procedures for Estimating and Allocating Area Source Emissions of Air Toxics. Springfield, Virginia. p. 7-3. March 1989.

Ward, D., and Wel Min Hao. “Air Toxic Emissions from Burning of Biomass Globally: Preliminary Estimates,” USDA Forest Service, Missoula, Montana. Presented at the 85th Annual Meeting and Exhibition of the Air and Waste Management Association, Kansas City, Missouri. June 21-26, 1992.

4.10.2 Open Burning of Scrap Tires

Process Description

Approximately 240 million vehicle tires are discarded annually (Lemieux and Ryan, 1993). Although viable methods for recycling exist, less than 25 percent of discarded tires are recycled; the remaining 175 million are discarded in landfills, stockpiles, or illegal dumps (Lemieux and Ryan, 1993). Although it is illegal in many states to dispose of tires using open burning, fires often occur at tire stockpiles and through illegal burning activities. It is estimated that approximately 7.5 million tires burn each year in landfills and illegal dumps in the United States (U.S. EPA, 1998). These fires generate a huge amount of heat and are difficult to extinguish; some tire fires continue for months. POM is emitted from these fires as a result of the incomplete combustion of the scrap tires.

Emission Factors

Table 4.10.2-1 contains emission factors for the open burning of tires (U.S. EPA, 1993). The average emission factor presented represents the average of tests performed on the simulated open burning of chunk and shredded tires. When estimating emissions from an accidental tire fire, it should be kept in mind that emissions from burning tires are generally dependent on the burn rate of the tire. A greater potential for emissions exists at lower burn rates, such as when a tire is smoldering rather than burning out of control (U.S. EPA, 1993). The fact that the shredded tires have a lower burn rate than whole tires indicates that the gaps between tire materials provide the major avenue of oxygen transport. Oxygen transport appears to be a major, if not the controlling mechanism for sustaining the combustion process (Lemieux and Ryan, 1993).

TABLE 4.10.2-1. PAH EMISSION FACTORS FOR OPEN BURNING OF SCRAP TIRES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1,000 tons tire (mg/kg tire)[a]	Emission Factor Range in lb/1,000 tons tire (mg/kg tire)	Emission Factor Rating
5-03-002-03	Simulated Open Burning of Chunk and Shredded Scrap Tires	None	Benz(a)anthracene	111.62 (55.81)	15.80 - 207.43 (7.90 - 103.71)	D
			Benzo(a)pyrene	288.96 (144.48)	230.32 - 347.60 (115.16 - 173.80)	D
			Benzo(b)fluoranthene	272.17 (136.09)	178.14 - 366.20 (89.07 - 183.10)	D
			Benzo(k)fluoranthene	382.04 (191.02)	200.48 - 563.60 (100.24 - 281.80)	D
			Chrysene	143.13 (71.57)	96.60 - 189.65 (48.30 - 94.83)	D
			Dibenz(a,h)anthracene	54.50 (27.25)	0.00 - 109.00 (20.00 - 54.50)	D
			Indeno(1,2,3-cd)pyrene	144.98 (72.49)	117.20 - 172.76 (58.60 - 86.38)	D
			Acenaphthene	3103.80 (1,551.90)	1,436.40 - 4,771.20 (718.20 - 2,385.60)	D
			Acenaphthylene	1138.29 (569.14)	1,136.17 - 1,140.40 (568.08 - 570.20)	D
			Benzo(ghi)perylene	197.04 (98.52)	72.40 - 321.68 (36.20 - 160.84)	D
			Anthracene	315.22 (157.61)	99.23 - 531.20 (49.61 - 265.60)	D
			Fluoranthene	505.65 (252.83)	84.60 - 926.69 (42.30 - 463.35)	D

(continued)

TABLE 4.10.2-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1,000 tons tire (mg/kg tire)[a]	Emission Factor Range in lb/1,000 tons tire (mg/kg tire)	Emission Factor Rating
5-03-002-03 (continued)	Simulated Open Burning of Chunk and Shredded Scrap Tires (continued)	None	Fluorene	232.89 (116.45)	86.80 - 378.98 (43.40 - 189.49)	D
			Naphthalene	490.85 (245.43)	0.00 - 981.69 (0.00 - 490.85)	D
			Phenanthrene	280.73 (140.37)	56.00 - 505.46 (28.00 - 252.73)	D
			Pyrene	188.69 (94.35)	70.40 - 306.98 (35.20 - 153.49)	D

[a] Emission factors are in expressed lb (mg) of pollutant per 1,000 tons (kg) of fuel burned.

Source: U.S. EPA, 1993.

Source Location

Open burning of scrap tires can occur at permitted landfills that stockpile scrap tires, at closed landfills that already contain scrap tires, and at illegal dumpsites where tires are discarded. The fires can start by accident or by arson, and it is unpredictable as to where and when they will occur.

SECTION 4.10.2 REFERENCES

Lemieux, P. M., and J. V. Ryan. "Characterization of Air Pollutants Emitted from a Simulated Scrap Tire Fire." Journal of the Air and Waste Management Association, Volume 43, pp. 1106-1115. August 1993.

U.S. Environmental Protection Agency. 1990 Emission Inventory of Section 112(c)(6) Pollutants: Polycyclic Organic Matter (POM), 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD)/2,3,7,8-Tetrachlorodibenzofuran (TCDF), Polychlorinated Biphenyl Compounds (PCBs), Hexachlorobenzene, Mercury, and Alkylated Lead. Emission Factor and Inventory Group, Research Triangle Park, North Carolina. Final Report. March 1998.

U.S. Environmental Protection Agency. Supplement F to Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. AP-42, Volume I, Supplement F. pp. 2.4-2 and 2.4-4. July 1993.

4.10.3 Agricultural Plastic Film Burning

Process Description

Large quantities of plastic film are commonly used for mulching, weed control, and to retain ground moisture in crop fields. When the crop residue is burned, the plastic film is also combusted. The plastic film is likely to be a combination of new or unused plastic (i.e., plastic that was not actually covering or underneath the crops or soil) and used plastic, which contains a high moisture and vegetation content. Each type of plastic burns differently. Used plastic is more difficult to ignite and burns at a much slower rate than new plastic. New or unused plastic is highly combustible and melts quickly to form a liquid pool that burns from the surface. Burning usually occurs in the crop row where the plastic is used or in large piles in the field where the plastic is collected (Linak et al., 1989).

Emission Factors

Table 4.10.3-1 presents PAH emission factors for the burning of agricultural plastic film (U.S. EPA, 1993). Factors are presented for two types of burning conditions. One set of factors is based on the plastic being gathered into a pile and burned. The second set of factors is based on the plastic being burned in a pile with a forced-air current supplied to simulate burning conditions in an air curtain. An air curtain is a portable or stationary combustion device that directs a plane of forced air so as to create a curtain of air around the pit where the plastic is burning. Air curtains are used in some states as a means of improving the combustion characteristics of control burns involving agricultural plastic. The factors represent the average of the emission rates for used and unused plastic. The test study on which both sets of emission factors are based used plastic that consisted primarily of polyethylene and carbon black (Linak et al., 1989).

TABLE 4.10.3-1. PAH EMISSION FACTORS FOR OPEN BURNING OF AGRICULTURAL PLASTIC FILM

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1000 tons (µg/kg)[a]	Emission Factor Range in lb/1000 tons (µg/kg)[a]	Emission Factor Rating
5-03-002-02	Simulated Open Burning of Agricultural Plastic Film (Pile Burn)	None	Benz(a)anthracene	6.72E-02 (33.57)	2.88E-02 - 1.06E-01 (14.41 - 52.73)	C
			Benzo(a)pyrene	4.93E-02 (24.65)	1.51E-02 - 8.35E-02 (7.53 - 41.76)	C
			Benzo(b)fluoranthene	4.39E-02 (21.94)	1.85E-02 - 6.93E-02 (9.25 - 34.63)	C
			Benzo(k)fluoranthene	1.63E-02 (8.13)	5.00E-03 - 2.75E-02 (2.51 - 13.74)	C
			Chrysene	7.22E-02 (36.08)	3.44E-02 - 1.10E-01 (17.18 - 54.98)	C
			Indeno(1,2,3-cd)pyrene	5.08E-02 (25.37)	2.14E-02 - 8.01E-02 (10.70 - 40.04)	C
			Benzo(ghi)perylene	6.44E-02 (32.43)	2.99E-02 - 9.89E-02 (14.93 - 49.93)	C
			Anthracene	8.45E-03 (4.23)	2.60E-03 - 1.43E-02 (1.32 - 7.14)	C
			Fluoranthene	4.20E-01 (210.07)	2.14E-01 - 6.26E-01 (107.05 - 313.08)	C
			Phenanthrene	8.45E-02 (42.23)	4.81E-02 - 1.21E-01 (24.05 - 60.40)	C
			Pyrene	2.62E-01 (131.04)	1.18E-01 - 4.07E-01 (58.81 - 203.26)	C
			Retene	5.12E-02 (25.58)	3.75E-02 - 6.48E-02 (18.77 - 32.38)	C

(continued)

TABLE 4.10.3-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1000 tons (µg/kg)[a]	Emission Factor Range in lb/1000 tons (µg/kg)[a]	Emission Factor Rating
5-03-002-02 (continued)	Simulated Open Burning of Agricultural Plastic Film (Pile Burn) (continued)	None	Benzo(e)pyrene	4.21E-02 (21.02)	1.93E-02 - 6.48E-02 (9.65 - 32.38)	C
5-03-002-02	Simulated Open Burning of Agricultural Plastic Film (Forced Air Burn)	None	Benz(a)anthracene	4.10E-03 (2.05)	2.40E-03 - 5.80E-03 (1.19 - 2.91)	C
			Benzo(a)pyrene	1.45E-03 (0.73)	0.00 - 2.90E-03 (0.00 - 1.45)	C
			Benzo(b)fluoranthene	2.55E-03 (1.26)	1.90E-03 - 3.20E-03 (0.93 - 1.59)	C
			Benzo(k)fluoranthene	6.50E-04 (0.33)	0.00 - 1.30E-03 (0.00 - 0.66)	C
			Chrysene	4.90E-03 (2.45)	2.40E-03 - 7.40E-03 (1.19 - 3.70)	C
			Indeno(1,2,3-cd)pyrene	2.80E-03 (1.39)	0.00 - 5.60E-03 (0.00 - 2.78)	C
			Benzo(ghi)perylene	2.10E-03 (1.06)	0.00 - 4.20E-03 (0.00 - 2.11)	C
			Anthracene	1.05E-03 (0.53)	8.00E-04 - 1.30E-03 (0.40 - 0.66)	C
			Fluoranthene	9.25E-02 (46.26)	7.82E-02 - 1.07E-01 (39.12 - 53.39)	C
			Phenanthrene	2.13E-02 (10.64)	1.74E-02 - 2.51E-02 (8.72 - 12.56)	C

(continued)

TABLE 4.10.3-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/1000 tons (µg/kg)[a]	Emission Factor Range in lb/1000 tons (µg/kg)[a]	Emission Factor Rating
5-03-002-02 (continued)	Simulated Open Burning of Agricultural Plastic Film (Forced Air Burn) (continued)	None	Pyrene	2.57E-02 (12.10)	1.19E-02 - 3.95E-02 (5.95 - 18.24)	C
			Retene	5.95E-03 (2.98)	5.80E-03 - 6.10E-03 (2.91 - 3.04)	C
			Benzo(e)pyrene	1.45E-03 (0.73)	0.00 - 2.90E-03 (0.00 - 1.45)	C

[a] Emission factors are expressed in lb (µg) of pollutant emitted per 1,000 tons (kg) of plastic film burned.

Source: U.S. EPA, 1993.

Source Location

The practice of burning agricultural plastic is likely to occur in rural areas, where the material is regularly used by farmers to cover field crops. Permits may or may not be issued for this type of open burning, and its occurrence could be affected by local regulations.

SECTION 4.10.3 REFERENCES

Linak, W. B., J. V. Ryan, E. P., R. W. Williams, and David M. DeMarini. "Chemical and Biological Characterization of Products of Incomplete Combustion from the Simulated Field Burning of Agricultural Plastic." Journal of the Air and Waste Management Association. Volume 39, No. 6, pp. 836-846. June 1989.

U.S. Environmental Protection Agency. Supplement F to Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. AP-42, Volume I, Supplement F. July 1993. pp. 2.4.14-2.4.19. 1993.

4.10.4 Coal Refuse Burning

Process Description

Coal as it comes from a mine contains various amounts of impurities such as mine waste, slate, shale, calcite, gypsum, clay, and pyrite. Together these wastes are referred to as coal refuse or gob. The gob or refuse is separated from coal prior to its being marketed and is commonly piled into banks or stored in impoundments near coal mines and coal preparation plants. Coarse refuse (i.e., greater than 595 μm diameter) is deposited into piles by dump trucks, mine cars, conveyors, or aerial trams. Indiscriminate dumping and poor maintenance of refuse piles are two practices that can result in spontaneous combustion of refuse piles (Chalekode and Blackwood, 1978). Because they are sources of highly inefficient combustion, burning coal refuse piles, outcrops, and mines have been identified as potential POM air emission sources (Chalekode and Blackwood, 1978; Kelly, 1983).

Spontaneous ignition and combustion of coal refuse piles and impoundments is mainly an oxidation phenomenon involving coal, associated pyrite, and impure coal substances. The oxidation of carbonaceous and pyrite material in the coal refuse is an exothermic reaction. The temperature of a coal refuse pile (or portions of it) increases if the amount of circulating air is sufficient to cause oxidation, but insufficient to allow for dissipation of the resulting heat. The temperature of the refuse pile then increases until ignition temperature is reached. Experimental evidence has indicated that the heat of wetting of coal is greater than the heat of oxidation of coal; therefore, the presence of moisture in air accelerates the self-heating process in coal refuse piles. For this reason, the relative humidity of ambient air is a key factor affecting coal refuse pile fires (Chalekode and Blackwood, 1978).

Coal textural moisture content (i.e., moisture retained in coal pores and void spaces) is also an important variable in the occurrence of coal refuse fires. Upon exposure to air, moisture is lost from the coal pores, leaving a significant area for oxygen adsorption. Increased oxygen adsorption facilitates greater oxidation and promotes the development of coal refuse pile fires (Chalekode and Blackwood, 1978).

Oxidation of pyrite impurities in coal refuse piles is another supplementary factor which enhances the possibility and severity of coal refuse combustion. Oxidation of pyrite is a highly exothermic reaction that increases the temperature of surrounding material and thus increases the rate of oxidation of the coal.

The spontaneous combustion of coal in outcrops and abandoned mines is also attributable to oxidation phenomena involving coal, moisture, and pyrite impurities. Other factors affecting combustion in mines and outcrops include coal rank, coal strata geology, and the coal strata temperature profile. Low-rank coals such as subbituminous or high-volatile bituminous are more susceptible to spontaneous combustion than a high-rank coal such as low-volatile bituminous or anthracite. Low-rank coals contain a greater amount of moisture and pyrite impurities than high-rank coals, which enhances their propensity for spontaneous combustion. The presence of faults in coal seams enhances oxidation by providing channels for greater volume and more distributed air flow. Coal strata temperature typically increases with depth. Oxidation rate, therefore, will increase with depth, making the seam more vulnerable to spontaneous combustion.

Various techniques exist to control emissions from burning coal refuse piles, outcrops, and mines. The majority of these techniques are based on eliminating the oxygen supply to extinguish the fire or on preventing the fire from spreading. The primary methods that have been applied to refuse piles are described below:

- <u>Isolation</u> - The burning area is isolated from the remainder of the refuse pile by trenches and is quenched with water or blanketed with incombustible material.
- <u>Blanketing</u> - Some piles are extinguished by leveling the top, then sealing the top and the sides with fine, incombustible material such as flyash, clay, quarry wastes, or acid mine drainage sludge. Heavy seals of such material are necessary to avoid erosion. The use of clay is limited as it cracks over hot spots, impairing the seal. A slurry of water and finely divided incombustible material, such as pulverized limestone, flyash, coal silt, or sand, is forced into the burning pile to provide some cooling action and also to fill the voids to prevent air from entering the pile.

- Explosives - Many burning piles have an impenetrable, ceramic-like, clinker surface which does not allow the penetration of slurries and water. In this case, explosive charges are placed deep into the bank through horizontally drilled holes. The explosion creates fissures in the fused covering material. Water is then applied through these crevices and the quenched material is loaded out.

- Spraying - In this method, water is sprayed over the entire refuse bank. However, this is only a temporary solution as the pile reignites with renewed vigor once the water spray is stopped.

- Accelerated Combustion and Quenching - The burning refuse material is lifted by a dragline and dropped through air into a water-filled lagoon 49 to 98 feet (15 to 30 m) below for the purpose of burning off the combustible material completely during the drop. Another dragline and bulldozers are used to remove the quenched material from the lagoon floor and compact it into a tight, dense fill material.

- Ponding - Retaining walls are constructed around the perimeter of a refuse bank after subdividing the surface into a series of discrete level areas and each area is filled with water to flood the fire. This may cause explosions due to the formation of water gas. Water penetration into the pile is poor.

- Cooling and Dilution - Water is sprayed on the burning pile from multiple nozzles and the cooled refuse is mixed, by bulldozer, in a one-to-one volume proportion with soil and/or burned-out refuse from a nearby area. The mixture is then compacted by heavy equipment.

- Hydraulic Jets - High velocity water cannons are used to quench the burning refuse material. The quenched material is then relayered and compacted by a dragline and bulldozer.

Emission Factors

PAH emission factors were found in the literature for coal refuse piles that are burning (Chalekode and Blackwood, 1978). These factors are listed in Table 4.10.4-1. In the referenced study, particulate POM emissions from a burning coal refuse pile were measured by

TABLE 4.10.4-1. PAH EMISSION FACTORS FOR COAL REFUSE BURNING

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/hr-ton (kg/hr-metric ton)[a]	Emission Factor Rating
A28-10-000-000	Coal Refuse Burning	None	Benz(a)anthracene/Chrysene	6.12E-09 (3.06E-09)	E
			Benzo(a)pyrene/ Benzo(e)pyrene/Perylene	3.91E-10 (1.95E-10)	E
			Benzo(k or b)fluoranthene	6.25E-10 (3.12E-10)	E
			Anthracene/Phenanthrene	5.08E-09 (2.54E-09)	E
			Fluoranthene	1.30E-09 (6.50E-10)	E
			Pyrene	1.20E-09 (5.98E-10)	E
			Benzo(c)phenanthrene	2.08E-10 (1.04E-10)	E
			Dibenzothiophene	1.04E-10 (5.20E-11)	E
			Dimethylbenzanthracenes (isomers)	3.00E-09 (1.50E-09)	E
			Methylanthracenes, -phenanthrenes	7.69E-09 (3.84E-09)	E
			9-Methylanthracene	2.08-10 (1.04E-10)	E

[a] Emission factors are in lb (kg) of pollutant emitted per hr-ton (hr-metric ton) of burning refuse.

Source: Chalekode and Blackwood, 1978.

using a high-volume filter air sampling device. The emission factors are based on test data from a single bituminous coal refuse pile that had been smoldering for the last 10 years. There were no control procedures identified for the sampled refuse pile.

As shown in Table 4.10.4-1, the following four compounds account for almost 84 percent of the measured POM emissions from the coal refuse pile: methylanthracenes/phenanthrenes (30 percent), chrysene/benz(a)anthracene (24 percent), anthracene/phenanthrene (20 percent), and dimethylbenzanthracenes [isomers] (12 percent). Other important PAHs, in terms of carcinogenicity, were also detected, but in much lesser quantities.

Source Locations

Burning or potentially-burning coal refuse piles are linked to coal mining and coal preparation plant locations. Recent information on the possible sources of burning refuse piles was obtained from the U.S. Bureau of Mines (U.S. Bureau of Mines, 1994). A list of states and Indian reservations where there are existing, unreclaimed gob piles and surface burning piles is presented in Table 4.10.4-2. Gob piles are coal refuse piles that may or may not be burning, but are generally of lower priority from a health standpoint because they not located in the vicinity of a large human population. Surface burning piles are a higher priority coal refuse pile that is actually burning and that is also in close proximity to a human population. The table lists the number of sites and the total number of acres for these sites for each state and Indian reservation in the country where data were available.

TABLE 4.10.4-2. UNRECLAIMED COAL REFUSE SITES AND ASSOCIATED ACREAGE

State/Tribe	Number of Gob[a] Sites	Gob Acres	Number of Surface Burning[b] Sites	Surface Burning Acres
Alaska	0	0.0	ND[c]	ND
Alabama	37	415.5	5	32.5
Arkansas	6	53.0	0	0.0
Blackfeet	1	0.5	ND	ND
Colorado	238	500.3	1	1.0
Crow	9	11.0	ND	ND
Georgia	1	4.0	ND	ND
Hopi	0	0.0	ND	ND
Iowa	3	3.0	0	0.0
Illinois	28	308.7	0	0.0
Indiana	51	495.3	0	0.0
Jicarilla Apache	0	0.0	ND	ND
Kansas	42	203.0	0	0.0
Kentucky	36	446.5	20	103.2
Maryland	4	11.0	1	3.0
Michigan	5	19.0	0	0.0
Missouri	38	118.8	0	0.0
Montana	0	0.0	0	0.0
Navajo	14	48.0	0	0.0
North Dakota	0	0.0	0	0.0
New Mexico	19	110.0	1	1.0
Ohio	55	753.0	3	77.0
Oklahoma	21	229.5	ND	ND
Oregon	1	5.0	ND	ND
Pennsylvania	60	1,207.0	19	75.9
Rocky Boys	1	1.0	ND	ND
San Carlos Apache	1	0.2	ND	ND

(continued)

TABLE 4.10.4-2. (Continued)

State/Tribe	Number of Gob[a] Sites	Gob Acres	Number of Surface Burning[b] Sites	Surface Burning Acres
Southern Ute	5	5.0	ND	ND
Tennessee	35	134.0	1	1.0
Texas	0	0.0	ND	ND
Uintah and Ouray	1	0.1	ND	ND
Utah	12	61.0	6.0	0
Virginia	131	364.0	5	19.9
Washington	10	8.0	0	0.0
West Virginia	241	2,514.5	26	112.3
White Mountain Apache	1	0.1	ND	ND
Wind River	12	11.6	ND	ND
Wyoming	1	5.0	0	0.0
Total Nationwide	1,120	8,047.1	82	432.8

[a] Gob refers to the refuse or waste removed from an underground mine and includes mine waste, rock, pyrites, slate, or other unmarketable materials which are separated during the cleaning process. Gob sites have the potential to burn, but may not be presently burning.

[b] Surface burning refers to any sites where there is continuous combustion of mine waste material resulting in smoke, haze, heat, or venting of hazardous gases within close distance to a populated area and presenting a danger to public health, safety, and general welfare.

[c] ND = no data reported.

Source: U.S. Bureau of the Mines, 1994.

SECTION 4.10.4 REFERENCES

Chalekode, P.K., and T.R. Blackwood. Source Assessment: Coal Refuse Piles, Abandoned Mines, and Outcrops - State of the Art. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio. EPA Report No. 600/2-78-004v. July 1978.

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. 5-3 to 5-9. 1983.

U.S. Bureau of the Mines. Abandoned Mine Land Inventory System. Branch of Technical Support, Division of Abandoned Mine Land Reclamation. Washington, DC. 1994.

4.10.5 Miscellaneous Open Burning

Process Description

The miscellaneous open burning category includes open burning activities not covered in the discussions on coal refuse banks, wildfires and prescribed burning, scrap tire burning, and agricultural plastic film burning. Types of open burning included in the miscellaneous category are: municipal refuse open burning; open burning of scrap automobile components (including the automobile body); open burning of waste railroad ties; and burning of landscaping refuse (grass clippings, leaves, and branches). The purpose of burning in most of these cases is volume reduction to facilitate final disposal of the waste material (Siebert et al., 1978). In the case of automobile body burning, burning is performed to expedite the recovery and recycling of usable metal in the automobiles by removing all organic materials (plastic, vinyl, etc.) (Kelly, 1983).

The procedure of open burning in any of the miscellaneous categories is relatively simple. The material to be burned (domestic trash, leaves, etc.) is collected and aggregated in an open space fully exposed to the atmosphere. The materials are ignited and allowed to burn and smolder until all combustible material is consumed or the desired degree of volume reduction is achieved. Combustion efficiency in such operations is typically poor. Potential POM emissions from such operations are highly variable because waste moisture content and combustion conditions (air flow, oxygen levels, waste configuration, degree of exposed surface area) are quite variable from site to site. In addition, some wastes may contain organic constituents that are precursors to POM compounds or that accelerate POM compound formation.

Generally, there are two means to control POM emissions from miscellaneous open burning--enclosure of the burning with exhaust ventilation to standard control devices and prohibition of open burning. In most areas of the United States, open burning of municipal refuse, automobiles, and grass, leaves, etc., has been greatly restricted, and in the case of municipal refuse and automobile components, completely prohibited. Open burning of grass and leaves has been controlled by requiring collection agencies and the general public to have permits for burning.

Emission Factors

The available emission factor data for open burning of municipal refuse automobiles, and landscaping refuse are presented in Table 4.10.5-1 (Hangebrauck et al., 1967). The data in Table 4.10.5-1 represent measured POM emission factors from tests conducted in a laboratory research facility designed to simulate and characterize open burning emissions. The laboratory experiments burned automobile components, municipal refuse, and landscaping refuse (Hangebrauck et al., 1967). The results of the laboratory open burning tests are presented as a function of the amount of waste burned. The factors could be determined for the laboratory open burning tests because all conditions of the tests such as emission rates, flow rates, waste throughput, etc., could be controlled. Conditions during actual open burning may not match the exact conditions in the laboratory tests, so the user should use caution in applying these factors.

Source Location

The sources of miscellaneous open burning are extremely varied and their location will depend on whether these activities are normally practiced in the local geographical area. Obviously, where such activities are prohibited there is likely to be little activity besides that associated with illegal burning. Burning of landscape refuse can take place at numerous residential sites and it may be difficult to get data on the quantity of refuse burned. In most cases, though, the user can assume a certain amount of waste generation per household or per capita for many of the categories in order to calculate a preliminary estimate of emissions.

TABLE 4.10.5-1. PAH EMISSION FACTORS FOR MISCELLANEOUS OPEN BURNING SOURCES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor lb/ton (g/Mg)[a]	Emission Factor Rating
5-03-002-02	Open Burning of Municipal Refuse	None	Benzo(a)pyrene	6.76E-04 (0.34)	E
			Anthracene	ND	E
			Benzo(ghi)perylene	3.09E-04 (0.15)	E
			Fluoranthene	3.23E-03 (1.61)	E
			Phenanthrene	ND	E
			Pyrene	3.54E-03 (1.76)	E
			Benzo(e)pyrene	4.64E-04 (0.23)	E
			Perylene	ND	E
			Anthanthrene	ND	E
			Coronene	ND	E
5-03-002-01	Open Burning of Landscaping Refuse	None	Benzo(a)pyrene	6.94E-04 (0.35)	E
			Anthracene	ND	E
			Benzo(ghi)perylene	3.23E-04 (0.16)	E
			Fluoranthene	2.23E-03 (1.11)	E
			Phenanthrene	ND	E

(continued)

TABLE 4.10.5-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor lb/ton (g/Mg)[a]	Emission Factor Rating
5-03-002-01 (continued)	Open Burning of Landscaping Refuse (continued)	None	Pyrene	3.45E-03 (1.72)	E
			Benzo(e)pyrene	3.09E-04 (0.15)	E
			Perylene	7.51E-05 (0.04)	E
			Anthanthrene	5.30E-05 (0.03)	E
			Coronene	ND	E
5-03-002-03	Open Burning of Scrap Automobile Components	None	Benzo(a)pyrene	5.74E-02 (28.67)	E
			Anthracene	6.27E-03 (3.13)	E
			Benzo(ghi)perylene	3.93E-02 (19.62)	E
			Fluoranthene	1.08E-01 (53.80)	E
			Phenanthrene	4.28E-02 (21.37)	E
			Pyrene	1.52E-01 (75.63)	E
			Benzo(e)pyrene	2.90E-02 (14.49)	E

(continued)

TABLE 4.10.5-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor lb/ton (g/Mg)[a]	Emission Factor Rating
5-03-002-03 (continued)	Open Burning of Scrap Automobile Components (continued)	None	Perylene	5.21E-03 (2.60)	E
			Anthanthrene	4.42E-03 (2.21)	E
			Coronene	4.82E-03 (2.40)	E

[a] Emission factors are expressed in lb (g) of pollutant per ton (Mg) of refuse burned.

ND - Designates that compound was not detected.

Source: Hangebrauk et al., 1967.

SECTION 4.10.5 REFERENCES

Hangebrauck, R.P. et al. Sources of Polynuclear Hydrocarbons in the Atmosphere. U.S. Department of Health, Education, and Welfare, Public Health Service, Cincinnati, Ohio. Public Health Service Report No. AP-33. pp. 14-18. 1967.

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. 5-93 to 5-95. 1983.

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, Pollutant Strategies Branch, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. Prepared under EPA Contract No. 68-02-2836. pp. 92-97. November 1978.

4.11 MOBILE SOURCES

This section discusses mobile sources of POM emissions, which include on-road vehicles, aircraft, locomotives, marine vessels, and non-road vehicles and equipment. Overall, mobile sources are a significant contributor to POM emissions due to the large amount of activity associated with onroad vehicles and the many non-road vehicle and equipment categories. The primary sources of POM emissions from all the mobile sources are the incomplete combustion of fuel in the internal combustion engines and the unburned fuel and lubricants used in the engines.

4.11.1 Onroad Vehicles

Source Description

The internal combustion engines of mobile sources emit gas-phase hydrocarbons and particulate organic material as products of incomplete combustion and as noncombusted (leaked) fuel, fuel additives, and lubricants. Some POM, such as the nitro derivatives, are formed after the exhaust is released to the atmosphere. Nitro-PAH is formed when PAH in the particulate reacts with NO_x in the exhaust. The emission rate of POM from vehicle exhausts is dependent on a large number of factors, including engine type, operating conditions, and composition of both fuel and lubricating oil (Baek et al., 1991).

After exhaust is released from a vehicle, it is diluted approximately 1,000-fold in the first few seconds and cools very rapidly (National Research Council, 1983). POM and other vapor-phase organic chemicals often condense on carbon nuclei and on other particles in the exhaust that are also products of incomplete combustion. POM emissions from gasoline engine vehicles with oxidation catalysts are generally sulfuric acid droplets less than 0.1 μm in diameter that have organic compounds adsorbed on their surfaces (National Research Council, 1983). Particulate emissions from diesel engines are predominately elemental carbon particles that form chains or clusters approximately 0.15 μm in diameter onto which the organic compounds are adsorbed (National Research Council, 1983).

POM compounds from vehicle engine exhaust are distributed between the vapor phase and the particle phase, generally in accordance with their vapor pressures. POM compounds containing two to four rings, such as naphthalene, are found primarily in the vapor or gas phase, and the heavier POMs, such as benzo(a)pyrene, are found predominantly on particles less than 1 μm in diameter (Pederson et al., 1980). The actual distribution of POM between the vapor phase and the particle phase will depend on the temperature and nature of the available adsorption surface (Siegl and Chladek, 1992). Historically, particulate POM emissions from mobile sources have generally been of the most interest; however, vapor-phase emissions are also important from a health perspective because they have a higher chemical reactivity during atmospheric transport. For example, the reaction of vapor-phase POM with hydroxyl radicals and NO_2 during atmospheric transport represents a major source of the nitro-substituted POM found in ambient air (Siegl and Chladek, 1992).

Emissions of POM from gasoline automobiles and trucks are influenced by a number of factors, such as air-to-fuel ratio; presence of emission controls; engine load; mode of operation; extent of deterioration; and fuel effects. Fuel effects include aromaticity, POM content, and the presence of additives or lubricants.

Changes in air-to-fuel ratios produce the largest effects on PAH emissions. Air-to-fuel ratios less than stoichiometric promote incomplete combustion and, therefore, increase emissions of CO and POM. It has been found that the amount of PAH in engine exhaust generally decreases with an increasing air-to-fuel ratio (i.e., leaner mixture) (Pederson et al., 1980). Leaner mixtures supply excess oxygen, resulting in more complete combustion and lower emissions of PAH. For example, it has been estimated that 30 times more benzo(a)pyrene is produced at a 10:1 air-to-fuel ratio than at a 14:1 ratio (National Research Council, 1972).

Noncatalyst automobiles have been shown to have higher emission rates than automobiles equipped with catalytic converters. Rogge et al. reported a 25-fold higher total PAH emission rate for autos without catalytic converters than for autos equipped with catalytic exhaust emission control devices (1405.5 µg/km versus 52.5 µg/km) (Rogge et al., 1993).

Westerholm et al. also reported dramatic decreases in POM emissions from vehicles equipped with catalytic converters (Westerholm et al., 1992).

The effect of vehicle operation mode is related to the air-to-fuel ratio. Cold-start operation will cause higher POM emissions because the engine is operating in a choked, or fuel-rich, condition. Higher engine load also may increase POM emissions during cold starts. Vehicle speed, a key variable in vehicle operation, is also suspected to affect POM emissions. Westerholm et al. reported that an increase in PAH emissions was found with higher cruising speeds (Westerholm et al., 1992).

The extent of deterioration, or mileage, of a vehicle has been shown to affect POM emission rates significantly, with increasing deterioration over a threshold level causing increased emission rates. Handa et al. estimated that average POM emission rates increase linearly with mileage above 12,000 miles (Handa et al., 1984). Increased oil consumption is a primary cause of the increased POM emissions with mileage. The higher quantity of oil in older, more worn cylinders provides more intermediates for POM formation, and POM becomes concentrated in the oil (National Research Council, 1983). Another cause of increased POM emissions with mileage is the formation of deposits in the combustion chamber. Total hydrocarbon emissions increase with mileage until the deposits become stabilized at several thousand miles (National Research Council, 1983).

Fuel composition affects PAH emissions from vehicles. A number of studies have shown that PAH emissions increase as the aromatic content of the fuel increases (Baek, 1991). However, there is uncertainty as to whether the PAHs emitted in vehicle exhaust represent those that survive the combustion process or those that were originally present in the fuel. Westerholm et al. reported an increase in vapor-phase and particulate-phase PAH emissions related to increases in fuel PAH input (Westerholm et al., 1988). Another study showed that PAH emissions from a direct injection diesel engine increased as the aromatic content of the fuel increased (Mills et al., 1984). Westerholm et al. also reported, however, that a large proportion of fuel PAH input (>95 percent) is decomposed in the combustion process and that a major part (>50 percent) of the emitted PAH is formed in the combustion process (Westerholm et al., 1988).

Diesel-fueled vehicles emit particulate emissions that primarily consist of combustion-generated soot in combination with a solvent-extractable hydrocarbon fraction. POM compounds are associated with the hydrocarbon fraction. Particulate POM emissions from diesel vehicles are generally higher than those from catalyst-equipped gasoline vehicles. Rogge et al. estimated that particulate POM emission rates were four times higher from diesel trucks than from catalyst-equipped gasoline vehicles (Rogge et al., 1993). The EPA has estimated that light-duty diesel engines emit from 30 to 100 times more particles than comparable catalyst-equipped gasoline vehicles (U.S. EPA, 1993).

Diesel particulate matter is attributable to the incomplete combustion of fuel hydrocarbons, the engine oil, and other unburned fuel components. The POM compounds adsorbed or condensed onto the surface of carbon particles (i.e., soot particles) in the diesel exhaust are sometimes referred to as the soluble organic fraction (SOF) of the particulate matter. A significant part of the SOF is unburned lubricating oil that is vaporized from the cylinder walls by the hot gases during the power stroke. The EPA estimates that 10 to 50 percent of the diesel particulates formed are from engine oil (U.S. EPA, 1990). Some of the heavier hydrocarbons in the fuel may come through unburned and condense on the soot particles. Mills et al. demonstrated that PAH emissions from a direct injection diesel engine increased as the aromaticity of the fuels was increased from 10 to 70 percent (Mills et al., 1984).

An existing control option for diesel engines that reduces diesel particulate emissions is the combined technology of turbocharging and intercooling. Most heavy-duty diesel engines have this technology, and it was required for virtually all engines in 1991. Catalytic converters for diesel vehicles are also under development for more widespread use as a control technology. These catalysts are very efficient in reducing emissions of particle-bound POM compounds by oxidizing a large part of the SOF (U.S. EPA, 1990). Another control technology being developed is trap oxidizers, which trap the diesel particulate matter and burn them after they collect on a filter. Fuel reformulations are also being given serious consideration because POM emissions can be reduced by reducing the aromatic hydrocarbon content of the fuel.

Nitro-PAH compounds (a subset of POM) have also been found in diesel particulate emissions (National Research Council, 1983). One study (Lewtas, 1988) identified 23 different NO_2-PAH in soot particle extracts from diesel engine exhaust. In the same study, only one NO_2-PAH (1-nitropyrene) was identified in gasoline engine exhaust samples. In Lewtas' study, 1-nitropyrene is by far the most abundant nitro-PAH in diesel exhaust (107 to 1,590 ppm, relative to the weight of the extract), followed by the nitrophenanthrene/anthracene isomers. Lang et al. (1981) also addressed the activity of POM in the exhaust by exposing POM to filtered exhaust. They found that the particulate can react with NO_x in exhaust to form nitro-PAH compounds.

Emission Factors

A large amount of the emissions testing data concerning POM emissions from motor vehicles dates back to the 1970s and early 1980s, with many of the vehicles tested in those studies spanning the model years of the late 1960s to the early 1970s. Many of the emission rates estimated as part of those studies are now outdated because of the turnover of the vehicle fleet. Since the time of those studies, leaded gasoline has been virtually phased out of use, the majority of gasoline vehicles on the roads are now equipped with catalytic converters for emissions control, emission standards have become stricter, and there have been major improvements in the engine efficiency and performance of vehicles. All of these changes have generally helped to reduce individual vehicle emissions, including POM emissions. These emissions reductions, however, have been somewhat offset by the increase in vehicle miles travelled (VMT) occurring in the United States. VMT increased approximately 40.6 percent between 1983 and 1990 (U.S. DOT, 1991).

The remainder of this section presents the latest available POM emission rate information for gasoline and diesel vehicles. Because emission rates for motor vehicles vary tremendously with operating conditions (e.g., speed, engine load, engine temperature), the results from a number of different studies are presented. The user should select those emission rates that best represent the conditions being modeled.

Emission factors for PAH were developed as part of a significant tunnel sampling program conducted at the Baltimore Harbor Tunnel in Maryland (Benner and Gordon, 1989). Particulate matter and gas-phase PAH samples were collected in exhaust rooms of the tunnel during 1985 and 1986. Individual PAHs were identified and quantified by liquid and gas chromatographic techniques. The study team developed PAH emission rates using a simple model to convert observed PAH concentrations (ng/m^3) in the tunnel exhaust room to emission rates of PAH (μg/km). The resulting emission factors, which include particulate- and gas-phase PAH, are shown in Table 4.11-1.

The emission factors shown in Table 4.11-1 represent “fleet-wide” emission factors because they include all vehicle types traveling through the tunnel during the sample period. The study concludes that tunnel samples are appropriate for estimating emission factors because they represent actual samples from hundreds of vehicles, as opposed to PAH emission factors that are based on combinations of single-vehicle data. The researchers estimated the vehicle fleet breakdown as follows: 57.1 percent light-duty gasoline vehicles with a three-way catalyst, 21.1 percent light-duty gasoline vehicles with no catalyst, and 6.3 percent light-duty gasoline vehicles with an oxidation catalyst; 1.6 percent heavy-duty gasoline vehicles with no catalyst; and 9.3 percent heavy-duty diesel vehicles and 4.5 light-duty diesel vehicles. The emission rates in Table 4.11-1 can be used with fleet-wide VMT estimates to estimate emissions for all vehicle types combined (Benner et al., 1989).

Particle-associated PAH compounds were measured for transient driving conditions by Westerholm et al. (Westerholm et al., 1992). The study determined that the driving conditions under which the vehicle engine is operated (i.e., speed and load) are important factors in PAH exhaust emissions. The results of that study show that PAH emissions increase with increased velocity and that they vary with changes in acceleration. It was also found that vehicles equipped with a three-way catalyst had substantial reductions in PAH exhaust emissions over noncatalyst vehicles.

TABLE 4.11-1. FLEETWIDE PARTICULATE AND GAS-PHASE PAH EMISSION FACTORS FOR ON-ROAD MOBILE SOURCES

SCC Number	Emission Source	Pollutant	Average Emission Factor in lb/mi (μg/km)[a]	Emission Factor Range in lb/mi (μg/km)[a]	Emission Factor Rating
22-01-000-000 and 22-30-000-000	Gasoline and Diesel On-Road Vehicles	Benz(a)anthracene	6.00E-09 (2.00)	1.50E-09 - 2.10E-08 (0.50 - 7.00)	C
		Benzo(a)pyrene	6.00E-09 (2.00)	9.00E-10 - 1.50E-08 (0.30 - 5.00)	C
		Chrysene/Triphenylene	9.00E-09 (3.00)	3.00E-09 - 2.70E-08 (1.00 - 9.00)	C
		Indeno(1,2,3-cd)pyrene	3.00E-09 (1.00)	1.20E-09 - 1.20E-08 (0.40 - 4.00)	C
		Anthracene	1.80E-08 (6.00)	9.00E-09 - 3.00E-08 (3.00 - 10.00)	C
		Benzo(ghi)perylene	6.00E-09 (2.00)	1.20E-09 - 1.80E-08 (0.40 - 6.00)	C
		Fluoranthene	2.40E-08 (8.00)	1.20E-08 - 4.20E-08 (4.00 - 14.00)	C
		Phenanthrene	1.14E-07 (38.00)	6.60E-08 - 1.29E-07 (22.00 - 64.00)	C
		Pyrene	2.40E-08 (8.00)	1.20E-08 - 4.20E-08 (4.00 - 14.00)	C
		Benzo(e)pyrene	3.00E-09 (1.00)	9.00E-10 - 1.20E-08 (0.30 - 4.00)	C
		Benzo(ghi)fluoranthene	6.00E-09 (2.00)	3.00E-09 - 1.50E-08 (1.00 - 5.00)	C
		Cyclopenta(cd)pyrene	1.20E-08 (4.00)	3.00E-09 - 2.70E-08 (1.00 - 9.00)	C

(continued)

TABLE 4.11-1. (Continued)

SCC Number	Emission Source	Pollutant	Average Emission Factor in lb/mi (µg/km)[a]	Emission Factor Range in lb/mi (µg/km)[a]	Emission Factor Rating
22-01-000-000 and 22-30-000-000 (continued)	Gasoline and Diesel Onroad Vehicles (continued)	3-Methylphenanthrene	4.20E-08 (14.00)	2.70E-08 - 6.60E-08 (9.00 - 22.00)	C
		1-Methylphenanthrenes	2.40E-08 (8.00)	1.50E-08 - 3.90E-08 (5.00 - 13.00)	C
		2-Methylanthracene	6.00E-09 (2.00)	3.00E-09 - 1.20E-08 (1.00 - 4.00)	C
		Benzo(b,j&k)fluoranthrene	9.00E-09 (3.00)	3.00E-09 - 3.00E-08 (1.00 - 10.00)	C

[a] Emission factors are expressed in lb (µg) of pollutant emitted per mile (km) driven.

Source: Benner et al., 1989.

Emission factors for particulate PAH for catalyst and noncatalyst gasoline-fueled vehicles tested by Westerholm et al., are shown in Table 4.11-2. The results are shown for the transient driving condition of acceleration from idle up to approximately 44 mph (70 kph) followed by deceleration to idle again. The driving pattern follows that of the U.S. Federal Test Procedure-75 (FTP-75) for warm engine operation. Factors are presented for noncatalyst vehicles and for vehicles with a three-way catalyst installed, both running on unleaded gasoline fuel (Westerholm et al., 1992).

In another study, Westerholm et al. estimated emission rates for gas-phase-associated PAH (Westerholm et al., 1988). The study included sampling of gas-phase PAH emissions from a 1984 Volvo 240 model vehicle with the catalyst removed. The results of the study were integrated over all three phases (cold-start, hot-transient, and hot-start) of the U.S. FTP-73 driving test pattern. The emission factors for gas-phase PAH for vehicles running on fuel corresponding to commercially available unleaded gasoline are shown in Table 4.11-3. One of the conclusions drawn by the authors of the study was that there is an increase in PAH emissions due to fuel PAH input; however, a major portion of the fuel PAH input (greater than or equal to 95 percent) is decomposed in the combustion process. They also concluded that a major part of PAH emissions (greater than or equal to 50 percent) is formed in the combustion process.

Siegl and Chladek, also measured gas-phase PAH in gasoline vehicle exhaust (Siegl and Chladek, 1992). The authors sampled emissions only for the hot-transient phase, referred to as “Bag 3,” of the U.S. FTP driving cycle. The vehicle tested was a 1987 model year production vehicle equipped with a catalyst. Emission factors for nine PAH were measured in both the pre-catalyst and post-catalyst exhaust. These emission factors are presented in Table 4.11-4. All nine of the PAHs tested were detected in the pre-catalyst exhaust, but only six were above the limit of quantitation. Seven of the nine PAH tested were detected in the post-catalyst exhaust. The authors reported that the major differences between their results and those from the Westerholm et al. (1988) study, primarily the much higher levels of naphthalene and biphenyl, may be due to the differences in the testing methods used. The Westerholm study used cryogenic trapping followed by a multi-step sample-handling procedure that may have resulted in the loss of the relatively volatile PAH species (Siegl and Chladek, 1992).

TABLE 4.11-2. PARTICULATE PAH EMISSION FACTORS FOR LIGHT-DUTY GASOLINE VEHICLES DURING THE WARM-ENGINE OPERATION FTP DRIVING CYCLE

SCC Number	Emission Source	Pollutant	Noncatalyst Emission Factor in lb/mi (µg/km)[a]	Catalyst Emission Factor in lb/mi (µg/km)[a]	Emission Factor Rating
22-01-001-000	Light-Duty Gasoline Vehicles	Benz(a)anthracene	2.97E-09 (0.991)	2.01E-10 (0.067)	D
		Benzo(a)pyrene	9.00E-10 (0.300)	3.06E-10 (0.102)	D
		Benzo(b,k)fluoranthene	3.27E-09 (1.089)	4.62E-10 (0.154)	D
		Chrysene/Triphenylene	2.52E-09 (0.840)	3.00E-10 (0.100)	D
		Indeno(1,2,3-cd)pyrene	8.34E-10 (0.278)	2.82E-10 (0.094)	D
		Anthracene	1.35E-10 (0.045)	6.00E-12 (0.002)	D
		Benzo(ghi)perylene	1.65E-09 (0.550)	2.97E-10 (0.099)	D
		Fluoranthene	1.98E-09 (0.660)	2.49E-10 (0.083)	D
		Phenanthrene	4.77E-10 (0.159)	6.00E-11 (0.020)	D
		Pyrene	2.70E-09 (0.900)	6.00E-11 (0.020)	D
		Benz(a)fluorene	2.34E-10 (0.078)	6.00E-12 (0.002)	D
		Benzo(e)pyrene	2.40E-09 (0.800)	4.20E-10 (0.140)	D
		Benzo(ghi)fluoranthene	3.30E-09 (1.100)	1.26E-10 (0.042)	D

(continued)

TABLE 4.11-2. (Continued)

SCC Number	Emission Source	Pollutant	Noncatalyst Emission Factor in lb/mi (µg/km)[a]	Catalyst Emission Factor in lb/mi (µg/km)[a]	Emission Factor Rating
22-01-001-000 (continued)	Light-Duty Gasoline Vehicles (continued)	Coronene	8.67E-10 (0.289)	1.68E-10 (0.056)	D
		Cyclopenta(cd)pyrene	9.00E-10 (0.300)	2.40E-11 (0.008)	D
		2-Methylanthracene	3.51E-10 (0.117)	6.00E-12 (0.002)	D
		Perylene	1.14E-10 (0.038)	3.00E-12 (0.001)	D
		1-Methylphenanthrene	2.10E-10 (0.070)	6.00E-12 (0.002)	D
		3-Methylphenanthrene	2.61E-10 (0.087)	6.00E-12 (0.002)	D
		4 and 9-Methylphenanthrene	9.30E-11 (0.031)	3.00E-12 (0.001)	D
		1-Methylpyrene	2.46E-10 (0.082)	3.00E-12 (0.001)	D
		2-Methylpyrene	5.28E-10 (0.176)	6.00E-12 (0.002)	D
		Indeno(1,2,3-cd)fluoranthene	6.90E-11 (0.023)	1.20E-11 (0.004)	D
		1-Nitropyrene	9.90E-10 (0.330)	4.20E-10 (0.140)	D

[a] Emission factors are expressed in lb (µg) of pollutant emitted per mile (km) driven.

Source: Westerholm et al., 1992.

TABLE 4.11-3. GAS-PHASE EMISSION FACTORS FOR NONCATALYST LIGHT-DUTY GASOLINE VEHICLES

SCC Number	Emission Source	Pollutant	Emission Factor in lb/mi (µg/km)[a]	Emission Factor Rating
22-01-001-000	Light-Duty Gasoline Vehicles	Benz(a)anthracene	3.30E-09 (1.10)	D
		Chrysene/Triphenylene	1.53E-09 (0.51)	D
		Acenaphthylene	8.40E-08 (28.00)	D
		Fluorene	1.26E-07 (42.00)	D
		Naphthalene	6.90E-08 (23.00)	D
		Anthracene	8.40E-08 (28.00)	D
		Fluoranthene	5.40E-08 (18.00)	D
		Phenanthrene	2.73E-07 (91.00)	D
		Pyrene	5.10E-08 (17.00)	D
		Benzo(ghi)fluoranthene	2.07E-09 (0.69)	D
		Biphenylene	2.49E-08 (8.30)	D
		Methylpyrene	9.60E-10 (0.32)	D

TABLE 4.11-3. (Continued)

SCC Number	Emission Source	Pollutant	Emission Factor in lb/mi (µg/km)[a]	Emission Factor Rating
22-01-001-000 (continued)	Light-Duty Gasoline Vehicles (continued)	1-Methylphenanthrenes	4.80E-08 (16.00)	D
		1-Methylanthracene	ND	D

[a] Emission factors are expressed in lb (µg) of pollutant emitted per mile (km) driven.

ND = not detected.

Source: Westerholm et al., 1988.

TABLE 4.11-4. GAS-PHASE PAH EMISSION FACTORS FOR LIGHT-DUTY GASOLINE VEHICLES DURING THE HOT-START TRANSIENT PHASE OF THE FTP DRIVING CYCLE

SCC Number	Emission Source	Pollutant	Noncatalyst Emission Factor in lb/mi (µg/km)[a]	Catalyst-Equipped Emission Factor in lb/mi (µg/km)[a]	Emission Factor Rating
22-01-001-000	Light-Duty Gasoline Vehicles	Anthracene	2.98E-09 (9.94E-01)	ND (ND)	D
		Fluoranthene	4.10E-09 (1.37E+00)	4.10E-09 (1.37)	D
		Fluorene	1.08E-08 (3.60)	ND (ND)	D
		Naphthalene	3.75E-06 (1249.01)	5.20E-07 (173.37)	D
		Phenanthrene	4.10E-09 (1.37E+00)	4.10E-09 (1.37)	D
		Pyrene	3.73E-09 (1.24)	4.10E-09 (1.37)	D
		Biphenyl	1.16E-07 (38.53)	1.04E-08 (3.48)	D
		1-Methylnaphthalene	7.27E-07 (242.35)	3.11E-08 (10.38)	D
		2-Methylnaphthalene	1.57E-06 (521.98)	6.47E-08 (21.56)	D

[a] Emission factors are expressed in lb (µg) of pollutant emitted per mile (km) driven.

ND = Not detected.

Source: Siegl et al., 1992.

SECTION 4.11.1 REFERENCES

Baek, S.O., R.A. Field, M.E. Goldstone, P.W. Kirk, and J.N. Lester. "A Review of Atmospheric Polycyclic Aromatic Hydrocarbons: Sources, Fate and Behavior." Water, Air, and Soil Pollution, Volume 60, pp. 279-300. 1991.

Benner, B. A., and G. E. Gordon. "Mobile Sources of Atmospheric Polycyclic Aromatic Hydrocarbons: A Roadway Tunnel Study." Environmental Sciences and Technology, Volume 23, No. 23, pp. 1269-1278. 1989.

Handa, T., T. Yamauchi, K. Sawai, T. Yamamura, Y. Koseki, and T. Ishii. "In Situ Emission Levels of Carcinogenic and Mutagenic Compounds from Diesel and Gasoline Engine Vehicles on an Expressway." Environmental Science and Technology. 18(12), pp. 895-902. 1984.

Lang, J.M., L. Snow, R. Carlson, F. Black, R. Zweidinger, and S. Tejada. "Characterization of Particulate Emissions from In-Use Gasoline-Fueled Motor Vehicles." Society of Automotive Engineers, Warrendale, Pennsylvania. SAE Paper 811186. 1981.

Lewtas, J. "Experimental Evidence for the Carcinogenicity of Air Pollutants." U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina. pp. 54-55. 1990.

Lewtas, J. "Genotoxicity of Complex Mixtures: Strategies for the Identification and Comparative Assessment of Airborne Mutagens and Carcinogens from Combustion Sources." Fundamental and Applied Toxicology, Volume 10, pp. 571-589. 1988.

Mills, G.A., J.S. Howarth, and G.A. Howard. Journal of Inst. Energy, p. 273. 1984.

National Research Council. Polycyclic Aromatic Hydrocarbons: Evaluation of Sources and Effects. Committee on Pyrene and Selected Analogues, Board on Toxicology and Environmental Health Hazards, Commission on Life Sciences, National Academy Press, Washington, DC. pp. 1-1 to 1-35. 1983.

National Research Council. Particulate Polycyclic Organic Matter. Committee on Biologic Effects of Atmospheric Pollutants. Division of Medical Sciences, National Academy of Sciences, Washington, DC. pp. 15-21. 1972.

Pederson, P.S., J. Ingwersen, T. Nielsen, and E. Larsen. "Effects of Fuel, Lubricant, and Engine Operating Parameters on the Emission of Polycyclic Aromatic Hydrocarbons." Environmental Science and Technology. 14(1):71-79. 1980.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass. "Sources of Fine Organic Aerosol 2. Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks." Environmental Sciences and Technology, Volume 27, No. 4, pp. 636-651. 1993.

Siegl, W. O., and E. Chladek. “Measurement of Gas-Phase Polycyclic Aromatic Hydrocarbons (PAH) in Gasoline Vehicle Exhaust.” Presented at the Symposium on Mechanisms and Chemistry of Pollutant Formation and Control from Internal Combustion Engines, American Chemical Society, Washington, DC. pp. 1499-1504. August 23-28, 1992.

U.S. Department of Transportation. Highway Statistics 1990. Federal Highway Administration, Washington, DC. FHWA-PL-91-003. p. 209. 1991.

U.S. Environmental Protection Agency. Motor Vehicle-Related Air Toxics Study. Office of Mobile Sources, Ann Arbor, Michigan. EPA-420-R-93-005. p. ES-29. 1993.

U.S. Environmental Protection Agency. Emissions Control Strategies for Heavy-duty Diesel Engines. Office of Mobile Source Air Pollution Control, Ann Arbor, Michigan. EPA-460/3-90-001. p. 41. 1990.

Westerholm, R. N., J. Almen, and H. Li. “Exhaust Emissions from Gasoline-Fuelled Light Duty Vehicles Operated in Different Driving Conditions: A Chemical and Biological Characterization.” Atmospheric Environment, Volume 26B, No. 1, pp. 79-90. 1992.

Westerholm, R. N., T. E. Alsberg, A. B. Frommelin, and M. Strandell. “Effect of Fuel Polycyclic Aromatic Hydrocarbon Content on the Emissions of Polycyclic Aromatic Hydrocarbons and Other Mutagenic Substances from a Gasoline-Fueled Automobile.” Environmental Sciences and Technology, Volume 22, No. 8, pp. 925-930. 1988.

4.11.2 Aircraft

Process Description

There are two main type of aircraft engines in use today: the turbojet and piston. A kerosene-like fuel is used in the jet engines, while gasoline is used for piston engines. The fuel combustion process in aircraft engines results in exhaust emissions to the atmosphere. Studies of aircraft exhaust have reported the presence of PAH compounds (Spicer et al., 1987; AESO, 1990).

The aircraft fleet in the United States totals about 198,000, including both civilian and military aircraft. In terms of number of aircraft, most of the fleet is made up of general aviation aircraft operated by single- and twin- piston engines. However, most of the fuel consumption and the associated emissions are from commercial jet transports and military aircraft (U.S. EPA, 1993). Most commercial jet transports have two, three, or four engines, while military aircraft range from single or dual engine fighters to multi-engine transports with either turbojet or turboprop engines.

The fuel combustion in jet engines is a continuous process that supplies heated, expanded gases which are forced through a turbine to drive an associated propeller (turboprop), or are expelled through the aft end of the engine to provide direct thrust (turbojet). Factors affecting emissions from these engines include engine type, fuel type, power setting, and fuel flow rate. These parameters can vary widely from aircraft to aircraft, especially between those used for civilian operations and those dedicated to military use.

PAH formation in a turbine engine occurs in the primary and secondary combustion zones. In the primary combustion zone, incompletely combusted fuel droplets with diameters of 50 to 200 μm lead to the formation of particulate matter which consists primarily of carbon particles. Oxidation in the secondary combustion zone leads to particles of about 0.01 to 0.1 μm. At the exit of the combustion chamber in the engine, agglomerated particles about 0.6 to 0.8 μm remain in the turbine exhaust. PAH compounds are bound to these particles.

Fuel type is an important parameter that affects the characteristics and quantity of emissions from aircraft. For example, JP-5 is a less volatile fuel than JP-4, and would be expected to have different emission characteristics. Changes in fuel composition may, therefore, affect PAH emissions from these sources. Testing performed by the U.S. Air Force has been done primarily with JP-4, but civil aircraft use Jet-A fuel, which is a less volatile fuel that tends to produce less smoke (U.S. EPA, 1993). It is possible that the smoke reduction may also equate to a reduction in toxics, including PAH, that are normally absorbed or condensed on the smoke particles.

Emission Factors

Few studies have developed emission factors specific to aircraft engine exhaust. Available information reports concentrations of various pollutants detected in the engine exhaust. Most of the emissions testing has been conducted by military organizations, and applicability to civil aircraft may not be direct due to the differences in type of fuel used. Existing data suggests that fuel composition is the major determinant of engine exhaust emissions.

The EPA summarized PAH concentrations in the exhaust gas from emissions testing conducted on two engine types: a CFM-56 engine using JP-5 fuel (representing commercial applications of a recent technology, fuel efficient, advanced emission abatement design) and an F-110 military aircraft engine using JP-4 fuel (U.S. EPA, 1997).
Table 4.11.2-1 presents the individual fractions of PAH relative to VOC which can be used with VOC emissions estimates to calculate individual PAH emissions. The PAH/VOC fractions were developed from concentration measurements for individual PAH species and VOC as reported in the EPA summary (U.S. EPA, 1997). The PAH/VOC fractions are provided for four modes of operation (idle, 30 percent power, 63 percent power, and intermediate) for the F-110 military aircraft engine. The intermediate mode relates to 100 percent of rated thrust. There are three modes of operation (idle, 30 percent power, and 80 percent power) covered by the CF-56 engine data. Depending on a specific airport facilities operations, the time spent by the aircraft in any one of these particular modes can vary.

TABLE 4.11.2-1. PAH EMISSION CONCENTRATIONS IN AIRCRAFT GAS TURBINE ENGINE EXHAUST

				PAH/VOC Concentration Fractions[a]						
SCC Number	Emission Source	Control Device	Pollutant	Idle	30% power	63% power	80% power	Intermediate	Emission Factor Rating[c]	Reference
22-75-001-000	Gas Turbine Engine in F-110 Military Aircraft Using JP-4 Fuel	None	Anthracene	3.09E-06	3.12E-06	6.57E-06	NA	6.54E-06	NA	U.S. EPA, 1997
			Benzo(a)anthracene	7.24E-07	9.30E-07	2.18E-06	NA	2.24E-06		
			Benzo(a)pyrene	1.27E-06	9.46E-07	2.54E-06	NA	2.37E-06		
			Benzo(g,h,i)perylene	7.58E-07	4.77E-07	2.01E-06	NA	2.72E-06		
			Chrysene	1.29E-06	2.91E-06	3.68E-06	NA	3.25E-06		
			Fluoranthene	1.16E-05	2.36E-05	2.61E-05	NA	2.69E-05		
			Naphthalene (g)	1.18E-04	1.88E-04	1.83E-04	NA	1.71E-04		
			Phenanthrene	3.35E-05	4.64E-05	1.07E-04	NA	8.78E-05		
			Pyrene	1.39E-05	2.36E-05	2.61E-05	NA	2.13E-05		
22-75-001-000	Gas Turbine Engine in CFM-56 Aircraft Using JP-5 Fuel	Emission Abatement Design	Anthracene	4.00E-07	1.09E-06	NA	1.46E-06	NA	NA	U.S. EPA, 1997
			Benzo(a)anthracene	5.28E-08	4.03E-06	NA	1.04E-06	NA		
			Benzo(a)pyrene	2.81E-08	2.55E-06	NA	7.47E-07	NA		
			Benzo(g,h,i,)perylene	4.67E-09	3.56E-07	NA	1.68E-07	NA		
			Chrysene	5.61E-08	4.29E-07	NA	2.02E-07	NA		
			Fluoranthene	8.25E-07	8.24E-06	NA	4.55E-06	NA		
			Naphthalene (g)	4.31E-04	7.98E-05	NA	4.74E-05	NA		
			Phenanthrene	3.64E-06	3.54E-05	NA	3.08E-05	NA		
			Pyrene	1.01E-06	6.76E-06	NA	3.64E-06	NA		

[a] Concentration ratios expressed as parts per million as carbon (ppbC) of PAH divided by ppbC VOC.
NA = not applicable; ratings are not applicable since relative concentrations, not emission factors, are presented.

Source: U.S. EPA, 1997.

Simplified emission factors for PAH were derived as part of the MOE Toxic and Chemical Emission Inventory for Ontario and North America (Johnson et al., 1990) and are shown in Table 4.11.2-2. The emission factors presented in that study were derived from 1979 data on PAH concentrations in the exhaust particulate from a small gas turbine engine burning conventional fuel. Emission factors were then derived in units of mass of pollutant per landing and takeoff cycle (LTO). An LTO consists of the following operating modes:

- Approach;
- Taxi/idle in;
- Taxi/idle out;
- Takeoff; and
- Climb out.

LTO data are available from annual Federal Aviation Authority (FAA) publications (e.g., Federal Air Traffic Activity and Airport Activity Statistics of Certified Route Air Carriers), and are the common form of activity level used for many inventory applications. The LTO cycle represents the emissions occurring in the air quality zone of interest (i.e., the LTO cycle typically occurs between ground level and the local inversion height).

Additional information on PAH emissions from aircraft have been reported. Kuhlman and Chuang, concluded that most PAH in the engine exhaust decrease in concentration as engine operating power increases. Exceptions to this were fluoranthene and pyrene, which persisted at a 30 percent engine power setting (Kuhlman and Chuang, 1989a). Naphthalene was by far the PAH with the highest concentration measured in the exhaust gas from the three jet turbine engines tested in that study. Concentrations for naphthalene ranged from 17.7 μg/m^3 to 2560 μg/m^3 (Kuhlman and Chuang, 1989b).

TABLE 4.11.2-2. PAH PARTICULATE EMISSION FACTORS FOR AIRCRAFT GAS TURBINE ENGINES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/LTO (mg/LTO)[a]	Emission Factor Rating[b]
22-75-020-000	Aircraft Gas Turbine Engine	None	Benz(a)anthracene	1.44E-06 (0.65)	U
			Benzo(a)pyrene	2.74E-06 (1.24)	U
			Chrysene	6.81E-06 (3.08)	U
			Anthracene	8.00E-06 (3.62)	U
			Benzo(ghi)perylene	3.58E-06 (1.62)	U
			Fluoranthene	8.20E-05 (37.10)	U
			Phenanthrene	1.06E-04 (47.80)	U
			Pyrene	9.55E-05 (43.20)	U
			Benzo(e)pyrene	7.96E-07 (0.36)	U

[a] Emission factors are expressed in lb (mg) of pollutant emitted per landing and take-off cycle (LTO).

[b] These factors are assigned a “U5” rating since the original test data on which they are based, and the derivation of the factors, was not reviewed.

Source: Johnson et al., 1990.

SECTION 4.11.2 REFERENCES

Aircraft Environmental Support Office (AESO). Toxic Organic Contaminants in the Exhaust of Gas Turbine Engines. Aircraft Environmental Support Office, Naval Aviation Depot, North Island, San Diego, California. AESO Report No. 12-90. September 1990.

Johnson, N.D., M.T. Schultz, 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. pp. 211-213. March 1990.

Kuhlman, M.R., and J.C. Chuang. Characterization of Chemicals on Engine Exhaust Particles. Battele Columbus Division, Columbus, Ohio. ESL-TR-88-50. p. 77. June 1989a.

Kuhlman, M.R., and J.C. Chuang. Characterization of Chemicals on Engine Exhaust Particles. Battele Columbus Division, Columbus, Ohio. ESL-TR-88-50. p. 40. June 1989b.

Spicer, C.W., M.W. Holdren, S.E. Miller, D.L. Smith, R.N. Smith, M.R. Kuhlman, and D.P. Hughes. Aircraft Emissions Characterization: TF41-A2, TF-30-P103, and TF30-P109 Engines. Tyndall Air Force Base, Florida. ESL-TR-87-27. December 1987.

U.S. Environmental Protection Agency. Memorandum from Rich Cook, Assessment and Modeling Division to Joe Touma, Office of Air Quality Planning and Standards, Subject: “PAH/VOC Emission Fractions for Aircraft.” National Vehicle and Fuel Emissions Laboratory, Ann Arbor, Michigan. March 18, 1997.

U.S. Environmental Protection Agency. Toxic Emissions from Aircraft Engines: A Search of Available Literature. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-453/R-93-028. July 1993.

4.11.3 Locomotives, Marine Vessels, and Other Non-road Vehicles and Equipment

Process Description

There are a variety of non-road vehicles and equipment types that can produce POM emissions from the fuel combustion in the engines that power them. Included among these are locomotives, marine vessels, and other non-road vehicles and equipment. The locomotives of concern for POM emissions are those that are powered by internal combustion diesel-fueled engines (as opposed to electric-powered locomotives, which receive their energy from a stationary point source utility plant). Marine vessels that have either diesel-fueled internal combustion engines or residual oil-fueled boilers are of concern regarding POM emissions. Included in "other non-road vehicle and equipment" are: lawn and garden equipment, recreational vessels, industrial equipment, construction equipment, agricultural equipment, and logging equipment. The other non-road vehicles and equipment have 2-stroke gasoline, 4-stroke gasoline, or diesel-powered internal combustion engines that can produce POM emissions.

Most non-road engines used on locomotives, marine vessels, and other non-road vehicles and equipment are not currently regulated for emissions. There are very few non-road engines with emission control devices. Like onroad mobile sources, all of these non-road engines produce diesel exhaust and gasoline exhaust particulate matter, a portion of which consists of POM.

Emission Factors

There has been no information collected on the emission rates of specific POM compounds found in the exhaust of non-road engines and vehicles. Particulate matter from non-road mobile sources is estimated to contribute a median of 1.8 percent of the total PM emission inventory in a typical nonattainment area (U.S. EPA, 1993). The two major equipment categories contributing are construction equipment and commercial marine equipment. The available PM emission factors for non-road vehicles and equipment are outdated. In some cases (such as where they based on the use of leaded gasoline), would be incorrect to use in deriving emission factors. These categories of non-road engines should be identified as potential sources of POM in any inventory study. Some of these sources are scheduled to be regulated in the future, which may produce emission testing data that can be used in deriving POM emission factor data.

SECTION 4.11.3 REFERENCES

U.S. Environmental Protection Agency. Motor Vehicle-Related Air Toxics Study. Office of Mobile Sources, Ann Arbor, Michigan. EPA 420-R-93-005. pp. 14-1 to 14-2. 1993.

4.12 MISCELLANEOUS SOURCES

4.12.1 Carbon Black Manufacture

Process Description

Carbon black is a major industrial chemical used primarily as a reinforcing agent in rubber compounds, especially tires (Serth and Hughes, 1980). The chemical carbon black consists of finely divided carbon produced by the thermal decomposition of hydrocarbons. The manufacture of carbon black is of potential concern for POM emissions because the predominant production process involves the combustion of natural gas and the high-temperature pyrolysis of aromatic liquid hydrocarbons.

Approximately 90 percent of all carbon black produced in the United States is manufactured by the oil-furnace process shown in Figure 4.12.1-1 (Serth and Hughes, 1980; Serth and Hughes, 1977). The process streams identified in Figure 4.12.1-1 are defined in Table 4.12.1-1. All oil-furnace carbon black plants are similar in overall structure and operation. The most pronounced differences in plants are primarily associated with the details of the decomposition furnace design and raw product processing (Serth and Hughes, 1980). Other processes used for carbon black production are thermal decomposition of natural gas and exothermic decomposition of acetylene (Serth and Hughes, 1977).

In the oil-furnace process, carbon black is produced by the pyrolysis of an atomized liquid hydrocarbon feedstock in a refractory-lined steel furnace. Processing temperatures in the steel furnace range from 2,408 to 2,804°F (1,320 to 1,540°C). The heat needed to accomplish the desired hydrocarbon decomposition reaction is supplied by the combustion of natural gas (Serth and Hughes, 1980).

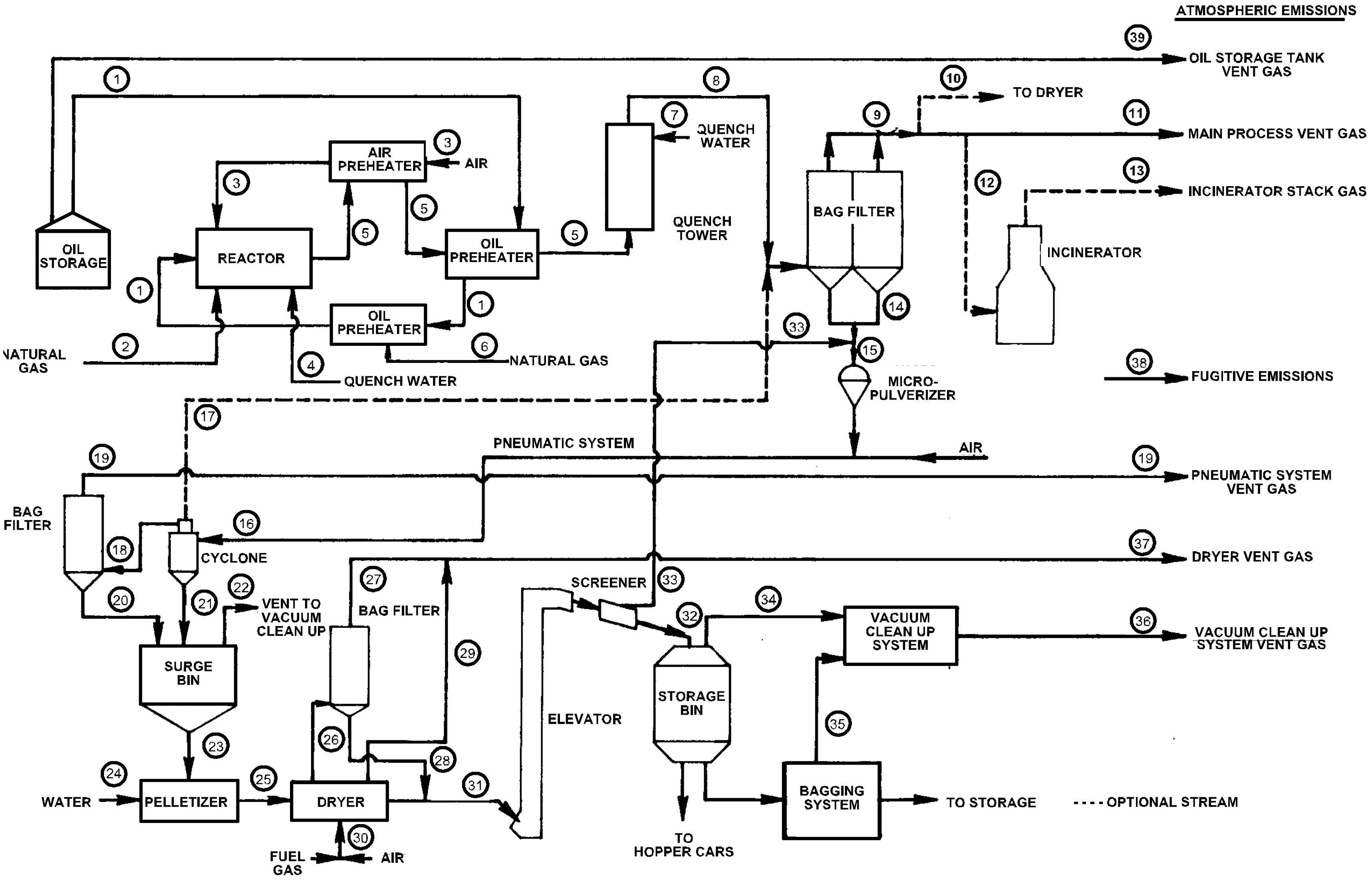


Figure 4.12.1-1. Process Flowsheet for an Oil-Furnace Carbon Black Plant

Source: Serth and Hughes, 1977.

TABLE 4.12.1-1. STREAM CODE FOR THE OIL-FURNACE PROCESS ILLUSTRATED IN FIGURE 4.12.1-1

Stream	Identification
1	Oil feed
2	Natural gas feed
3	Air to reactor
4	Quench water
5	Reactor effluent
6	Gas to oil preheater
7	Water to quench tower
8	Quench tower effluent
9	Bag filter effluent
10	Vent gas purge for dryer fuel
11	Main process vent gas
12	Vent gas to incinerator
13	Incinerator stack gas
14	Recovered carbon black
15	Carbon black to micropulverizer
16	Pneumatic conveyor system
17	Cyclone vent gas recycle
18	Cyclone vent gas
19	Pneumatic system vent gas
20	Carbon black from bag filter
21	Carbon black from cyclone
22	Surge bin vent
23	Carbon black to pelletizer
24	Water to pelletizer
25	Pelletizer effluent
26	Dryer direct heat source vent
27	Dryer bag filter vent
28	Carbon black from dryer bag filter
29	Dryer indirect heat source vent
30	Hot gases to dryer

(continued)

TABLE 4.12.1-1. (Continued)

Stream	Identification
31	Dried carbon black
32	Screened carbon black
33	Carbon black recycle
34	Storage bin vent gas
35	Bagging system vent gas
36	Vacuum cleanup system vent gas
37	Dryer vent gas
38	Fugitive emissions
39	Oil storage tank vent gas

Source: Serth and Hughes, 1980.

Feed materials used in the oil-furnace process consist of petroleum oil, natural gas, and air. Also, small quantities of alkali metal salts may be added to the oil feed to control the degree of structure of the carbon black (Serth and Hughes, October 1977). The ideal raw material for the production of modern, high-structure carbon black is an oil that is highly aromatic; low in sulfur, asphaltenes and high molecular weight resins; and substantially free of suspended ash, carbon, and water. The reactor for the oil furnace process consists of a refractory-lined steel furnace 4.9 to 29.5 feet (1.5 to 9 m) in length with an internal diameter of 0.49 to 2.5 feet (0.15 to 0.76 m).

To provide maximum efficiency, the furnace and burner are designed to separate, insofar as possible, the heat-generating reaction from the carbon-forming reaction. Thus, the natural gas feed (Stream 2 in Figure 4.12.1-1) is burned to completion with preheated air (Stream 3) to produce a temperature of 2,408 to 2,804°F (1,320 to 1,540°C). The reactor is designed so that this zone of complete combustion attains a swirling motion, and the oil feed (Stream 1), preheated to 392 to 698°F (200 to 370°C), is sprayed into the center of the zone. Oil preheating is accomplished by heat exchange with the reactor effluent and/or by means of a gas-fired heater. The oil is cracked to carbon and hydrogen, with side reactions producing carbon oxides, water, methane, acetylene, and other hydrocarbon products. The heat transfer from the hot combustion gases to the atomized oil is enhanced by highly turbulent flow in the reactor (Serth and Hughes, 1977).

The reactor converts 35 to 65 percent of the feedstock carbon content to carbon black, depending on the feed composition and the grade of black being produced. The yields are lower for the smaller particle size grades of black. Variables that can be adjusted to produce a given grade of black include operating temperature, fuel concentration, space velocity in the reaction zone, and reactor geometry (which influences the degree of turbulence in the reactor).

The hot combustion gases and suspended carbon black are cooled to about 1,004°F (540°C) by a direct water spray in the quench area, which is located near the reactor outlet. The reactor effluent (Stream 5 in Figure 4.12.1-1) is further cooled by heat exchange in the air and oil preheaters. It is then sent to a quench towers where direct water sprays finally reduce the stream temperature to 446°F (230°C).

Carbon black is recovered from the reactor effluent stream by means of a bag filter unit. The exhaust gas from the bag filter unit (Stream 9 in Figure 4.12.1-1) is vented directly to the atmosphere in most carbon black plants. Alternatively, it may be sent to a flare or incinerator to reduce contaminant loading (Stream 12). In addition, 13 to 15 percent of the effluent (Stream 10) may be diverted to produce auxiliary fuel for the raw product drying operation.

The raw carbon black collected in the bag filter unit must be further processed to become a marketable product. After passing through the pulverizer, the black has a bulk density of 24 to 59 kg/m^3, and it is too fluffy and dusty to be transported. It is therefore converted into pellets or beads with a bulk density of 97 to 171 kg/m^3. In this form, it is dust-free and sufficiently compacted for shipment.

Rotating horizontal drums operating at 374 to 392°F (190 to 230°C) are typically used for product drying in carbon black processes. The dryers are fueled by natural gas, which may be augmented by a portion of the main process vent gas. From 35 to 70 percent of the combustion gas is charged directly to the interior of the dryer. After passing through the dryer, this stream (Stream 26) is sent to a bag filter for removal of entrained carbon black before being vented to the atmosphere. The remaining 30 to 65 percent of the combustion gas (Stream 29) acts as an indirect heat source for the dryer and is vented directly to the atmosphere.

The dried, pelletized carbon black (Stream 31) is screened and sent to a covered storage bin via a bucket elevator. Oversize pellets are removed in the screener and recycled (Stream 33) to the pulverizer. From the product storage bin, the carbon black can be loaded into railroad hopper cars for bulk shipment or sent to a vacuum bagging system that is hermetically sealed to prevent emission of carbon black (Serth and Hughes, 1977).

Exhaust gas from the bag filter unit constitutes the main process vent and the largest source of POM emissions. About two-thirds of U.S. carbon black plants treat the bag filter exhaust stream to control CO and hydrocarbon emissions. Combustion in thermal incinerators, flares, or CO boilers is used for treating the gases. In the remaining facilities, bag filter exhaust emissions are vented directly to the atmosphere (Kelly, 1983). Emissions from product dryers are predominantly controlled by high-efficiency bag filter units; however, water scrubbers are also used at a few facilities (Serth and Hughes, 1977).

POM emissions associated with raw carbon black production (exclusive of additional processing steps) appear to be a function of the efficiency of the product recovery bag filter and, where applicable, the destructive or potentially constructive effect of hydrocarbon and CO combustion control devices. Because decreased efficiency in the product recovery bag filter unit means decreased carbon black production and lost revenues, it is likely that companies maintain these bag filters maintained at optimum conditions. The use of combustion control devices would be expected to reduce POM emissions by them into constituent compounds and elements (water, CO_2, nitrogen). Some investigators have speculated that POM compounds are being formed in the high temperature zone of the hydrocarbon and CO control devices but did not supply data to support this POM formation theory (Serth and Hughes, 1980).

Emission Factors

Several emission factors for POM emissions from carbon black manufacturing were identified in the literature. All identified emission factors are applicable to emissions from the main process vent. No emissions data of any type were available for potential POM sources associated with raw product processing such as grinding, drying, and packaging.

A well-documented source of uncontrolled main process vent PAH emission factors from carbon black manufacturing are those developed by Serth and Hughes (1980). Uncontrolled POM emissions from the main process vent (product recovery baghouse) were measured in a series of three tests, with the average emission factor for total POM being 0.0039 lb/ton (0.002 kg/Mg) of carbon black produced. Of the total 1,900 mg POM, 42 percent was acenaphthylene, 26 percent was pyrene, and 12 percent was methyl- and dimethylanthracenes/phenanthrenes. Mean PAH emission factors are presented in Table 4.12.1-2.

All POM sampling in the Serth and Hughes work was conducted using EPA Modified Method 5. Both vapor phase and particulate POM were quantified. Johnson, et al. (1990) presented emission factors for individual PAH species from the entire oil-furnace carbon black production process (Table 4.12.1-3). Emission factors were derived for material handling operations and furnace process fugitives using measured carbon black PAH concentrations and an EPA particulate emission factor of 1.06 lb/ton (0.53 kg/Mg) (Nishioka et al., 1986). The resulting emission factors were summed with the main process vent emission factors cited in Serth and Hughes, (1980) to represent the entire carbon black production process. Included in the aggregate emission factors are the transport air vent, pellet drying, bagging and loading operations, furnace process fugitives, and main process vent emissions. Emission factors were calculated assuming all fugitive PM emitted from the carbon black production process was in the form of carbon black (Johnson et al., 1990).

Source Locations

As of January 1993, there were 24 known carbon black manufacturing facilities in the United States. Over 75 percent of all carbon black production occurs in the states of Texas and Louisiana (36 and 40 percent, respectively). The location of all facilities and their estimated annual production capacities in 1985 are provided in Table 4.12.1-4 (SRI, 1993).

TABLE 4.12.1-2. PAH EMISSION FACTORS FOR OIL FURNACE CARBON BLACK MANUFACTURING: MAIN PROCESS VENT

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-01-005-04	Main Process Vent	None	Benz(a)anthracene/Chrysene	1.80E-05 (9.00E-06)	E
			Benzopyrenes and perylene	6.00E-05 (3.00E-05)	E
			Benzofluoranthenes	6.00E-05 (3.00E-05)	E
			Dibenzanthracenes	<4.00E-06 (<2.00E-06)	E
			Indeno(1,2,3-cd)pyrene	<4.00E-06 (<2.00E-06)	E
			Acenaphthylene	1.60E-03 (8.00E-04)	E
			Anthracene/Phenanthrene	1.40E-04 (7.00E-05)	E
			Benzo(ghi)perylene/Anthanthrene	4.60E-05 (2.30E-05)	E
			Fluoranthene	1.20E-04 (6.00E-05)	E
			Dimethylanthracenes/Phenanthrenes	2.80E-04 (1.40E-04)	E
			Pyrene	1.00E-03 (5.00E-04)	E
			Benzo(c)phenanthrene	<4.00E-06 (<2.00E-06)	E

(continued)

TABLE 4.12.1-2. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-01-005-04 (continued)	Main Process Vent (continued)	None	Benzo(ghi)fluoranthene	8.00E-05 (4.00E-05)	E
			Dibenzo(c,g)carbazole	<4.00E-06 (<2.00E-06)	E
			Dibenzopyrenes	<4.00E-06 (<2.00E-06)	E
			Dibenzothiophene	2.80E-05 (1.40E-05)	E
			7,12-Dimethyl(a)anthracene	1.40E-04 (7.00E-05)	E
			Methylanthracenes/Phenanthrenes	2.00E-04 (1.00E-04)	E
			Methylcholanthracene	<4.00E-06 (<2.00E-06)	E
			Methylfluoranthene/Pyrene	4.60E-05 (2.30E-05)	E

[a] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of carbon black produced.

Source: Serth and Hughs, 1980.

TABLE 4.12.1-3. PAH EMISSION FACTORS FOR OIL FURNACE CARBON BLACK MANUFACTURING: TOTAL PROCESS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-01-005-04, -06, -07, -08, -09	Total Process	None	Benz(a)anthracene	1.66E-05 (8.30E-06)	E
			Benzo(a)pyrene	2.86E-04 (1.43E-04)	E
			Benzofluoranthenes	1.88E-04 (9.40E-05)	E
			Chrysene	3.40E-05 (1.70E-05)	E
			Acenaphthylene	1.60E-03 (8.00E-04)	E
			Fluoranthene	1.06E-03 (5.30E-04)	E
			Phenanthrene	2.56E-04 (1.28E-04)	E
			Pyrene	1.60E-03 (8.00E-04)	E
			Benzo(e)pyrene	2.20E-04 (1.10E-04)	E
			Cyclopenta(cd)pyrene	7.40E-05 (3.70E-05)	E
			Dibenzothiophene	8.20E-05 (4.10E-05)	E
			Methylanthracenes/Methylphenanthrenes	2.00E-04 (1.00E-04)	E

(continued)

TABLE 4.12.1-3. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-01-005-04, -06, -07, -08, -09	Total Process	None	Perylene	1.42E-04 (7.10E-05)	E
			Triphenylene	1.00E-06 (5.00E-07)	E

[a] Emission factors are in lb (kg) of pollutant emitted per ton (Mg) of carbon black produced.

Source: Johnson et al., 1990.

TABLE 4.12.1-4. LOCATION AND ANNUAL CAPACITIES OF CARBON BLACK PRODUCERS IN 1993

Company	Facility Location	Annual Capacity, MM lb (MM kg)
Cabot Corporation	Franklin, LA	260 (118)
	Pampa, TX	60 (27)
	Villa Platte, LA	280 (127)
	Waverly, WV	180 (82)
Chevron Corporation	Cedar Bayou, TX	20 (9)
Columbian Chemicals Company	El Dorado, AR	110 (50)
	Moundsville, WV	180 (82)
	North Bend, LA	240 (109)
	Ulysses, KS	80 (36)
Degussa Corporation	Arkansas Pass, TX	130 (59)
	Belpre, OH	140 (64)
	New Iberia, LA	240 (109)
Ebonex Corporation	Melvindale, MI	8 (4)
General Carbon Company	Los Angeles, CA	1 (0.5)
Hoover Color Corporation	Hiwassee, VA	1 (0.5)
J.M. Huber Corporation	Baytown, TX	225 (102)
	Borger, TX	175 (79)
	Orange, TX	135 (61)
Sid Richardson Carbon and Gasoline Company	Addis, LA	145 (66)
	Big Springs, TX	115 (52)
	Borger, TX	275 (125)
Witco Corporation	Phoenix City, AL	60 (27)
	Ponca City, OK	255 (116)
	Sunray, TX	120 (54)
TOTAL		3,435 (1,558)

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 POM emissions from any given facility are a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

Source: SRI, 1993.

SECTION 4.12.1 REFERENCES

Johnson, N.D., M.T. Schultz, 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. 93. 1990.

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. 5-85 to 5-88. 1983.

Nishioka, M., H. Chang, and M.L. Lee. “Structural Characteristics of Polycyclic Aromatic Hydrocarbon Isomers in Coal Tars and Combustion Products.” Environ. Sci. Technol. 20(10). pp. 1023 - 1027. 1986.

Serth, R.W., and T.W. Hughes. “Polycyclic Organic Matter (POM) and Trace Element Contents of Carbon Black Vent Gas.” Environmental Science and Technology. 14(3):298-301. March 1980.

Serth, R.W., and T.W. Hughes. “Source Assessment: Carbon Black Manufacture.” U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. EPA Report No. 600/2-77-107k. October 1977.

SRI International. 1993 SRI Directory of Chemical Producers - United States of America. Menlo Park, California. p. 509. 1993.

4.12.2 Wood Treatment/Wood Preserving

Process Description

Creosote impregnation plants, also called wood treatment plants, have been identified as potential air emission sources of POM because creosote contains significant quantities of POM compounds. Creosote is a product of the fractional distillation of coal tar, which is a byproduct of bituminous coal coking. The principal use of creosote is as a wood preservative. It is used to treat crossties, switch ties, utility poles, crossarms, marine and foundation pilings, construction lumber, and fence posts (Wallingford and Que Hee, 1985). Other wood treatment/preservation processes using pentachlorophenol and chromated copper arsenate have not been identified as sources of POM emissions.

Creosote wood treatment is accomplished by either pressure or non-pressure processes. To initiate either process, wood products are debarked, sawed, and conditioned. Conditioning primarily involves the removal of moisture from the wood to enhance the penetration and retention of the preservative. Moisture reduction conditioning may be accomplished by outdoor storage (air seasoning) or by artificial conditioning processes. To expedite certain treatment processes, the wood may be pierced by knives (a process called incising) to provide avenues for penetration of the preservative solutions (U.S. Department of Agriculture, 1980).

The three primary methods of conditioning used in the wood treatment industry are steaming-and-vacuum, boiling-under-vacuum (the Boulton process), and vapor drying (Vaught and Nicholson, 1989).

The steaming-and-vacuum conditioning process involves the steaming of wood in the treatment cylinder (retort) for several hours at approximately 245°F (118°C). Following steaming, a vacuum is applied to the cylinder, causing moisture removal by mechanical and evaporative mechanisms.

A generic flow diagram of a wood preserving facility using the Boulton conditioning process is presented in Figure 4.12.2-1. In the Boulton (boiling-under-vacuum) process, the treatment cylinder containing timbers is filled with hot preservative oil. The cylinder is kept heated while a vacuum is applied. The heat causes a lowering of the boiling point of the water in the wood, resulting in evaporation. Evaporated moisture from the wood and vapors from the hot preservative oil are passed through a condenser to recover preservative via oil/water separation. The Boulton process has several advantages over other conditioning processes, including lower temperature requirements, minimal impact on wood strength and physical condition, and a greater moisture reduction capacity than the steaming process (Vaught and Nicholson, 1989).

The vapor-drying process uses a boiling organic solvent such as xylene to vaporize moisture from the wood during condensation. As the organic vapors condense, latent heat is given up, causing vaporization of water. Water and solvent vapors are passed through a condenser to recover solvent.

Ninety-five percent of all treated wood is preserved through pressurized processes. These processes involve the application of pneumatic or hydrostatic pressure to expedite the movement of preservative liquid into the wood. In the normal application of preservatives (e.g., creosote), wood is first loaded onto trams and introduced into the pressure vessel. In the pressure vessel, wood can be creosote pressure-treated by either the full-cell or the empty-cell process (U.S. Department of Agriculture, 1980).

In the full-cell process, an initial vacuum is applied to the charge for a period of about 30 minutes. At the end of this period, and while still maintaining the vacuum, the vessel is filled with creosote. The vacuum is then released and pressures of 50 to 250 psi are applied to the system. Pressure is maintained until the required gross absorption of preservative has been achieved. At the end of the pressure cycle, the pressure is reduced to atmospheric levels and the preservative liquid in the vessel is returned to storage. The treated wood will often be subjected to a final vacuum to remove excess preservative on the surface of the wood. Upon completion, the vacuum is released, the door of the vessel is opened, and the treated stock is removed.

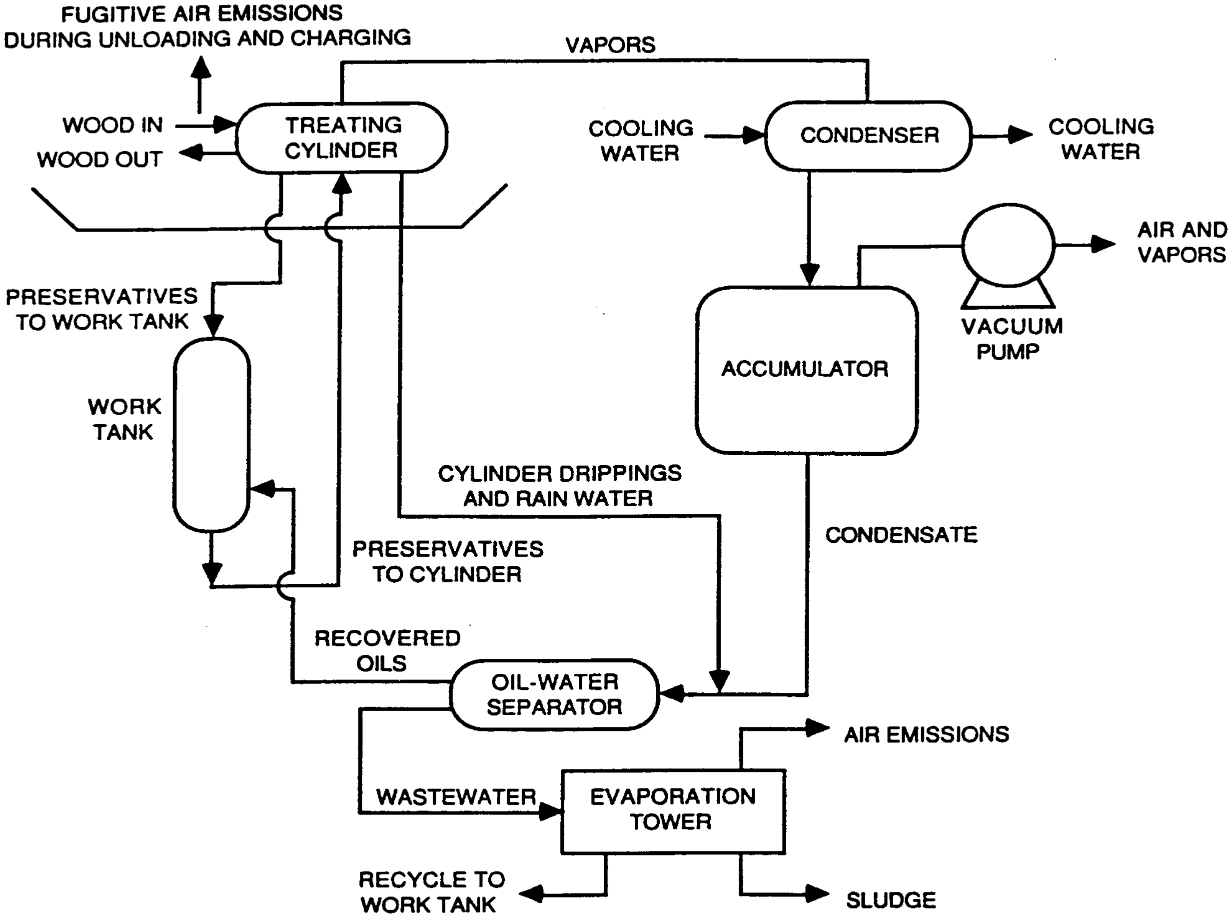


Figure 4.12.2-1. Flow Diagram of a Wood Preserving Facility Using the Boulton Conditioning Process

Source: U.S. EPA, 1988.

Creosote retentions achieved by the full-cell process vary from 20 to 30 lb/ft^3 (320 to 480 kg/m^3) (U.S. Department of Agriculture, 1980).

The objective of the empty-cell process is to obtain deep preservative penetration with relatively low total retention. In the process, the treatment retort is filled with preservative while either at ambient pressure conditions or under an initial air pressure of 25 to 100 psi, depending on the net retention of preservative desired and the resistance of the wood. After preservative has been added to the cylinder, the treatment pressure is elevated and maintained for a period of time. The expansive force of compressed air acts to drive out some of the preservative absorbed during the treatment process (Vaught and Nicholson, 1989). The remainder of the treating process is the same as that described for the full-cell process. Depending on the specifications of the customer, wood preservative retentions achieved by the empty-cell process range from 6 to 12 lb/ft^3 (96 to 208 kg/m^3) (U.S. Department of Agriculture, 1980).

In both the full-cell and empty-cell processes, creosote may be applied in an undiluted form or it may be diluted with coal tar or petroleum. Treatment using mixtures of creosote and heavy oils (i.e., No. 6 Oil) is referred to as the diluent process (Ebasco, 1989). Application temperatures for creosote and its solutions range from 210 to 230°F (99 to 110°C).

Products such as marine pilings are always treated by the full-cell process. Utility poles, crossties, and fence posts are routinely treated by the empty-cell process. The amount of preservative retention needed and the treatment process required are determined by the biological hazard to which the treated wood will be subjected in service. Creosote is also used as a restricted use pesticide (Ware, 1996).

Non-pressurized wood treatment processes are used commercially. Creosote use by individual consumers is restricted to those who are licensed applicators (Ware, 1996).

Generally, wood treated by non-pressure processes must be seasoned to a moisture content of 30 percent or less prior to treatment to provide the best results (U.S. Department of Agriculture, 1980).

Most commercial non-pressure creosote treatments are applied by cold-soak or thermal processes. In both processes, wood is exposed to the preservative in an open vessel. The principle behind the cold-soak process simply entails soaking seasoned wood in the preservative for a fixed period of time or until a predetermined gross retention has been achieved. The thermal process involves exposing wood to hot creosote for 6 to 12 hours followed by exposure to the preservative at ambient temperature for 2 hours (U.S. Department of Agriculture, 1980).

The creosote wood treatment source category is a source of primarily fugitive POM emissions that are associated with the actual treatment process and, to a greater degree, the handling of creosote raw materials and treated products. Fugitive emissions from treatment occur when the treatment vessel is opened at the end of the cycle. The duration of such emissions from each vessel is relatively short because vessels are only opened once or twice during each working shift (Wallingford and Que Hee, 1985; Andersson et al., 1983).

Fugitive POM emissions may occur during creosote transfer from an incoming tanker or rail car to plant storage facilities. The method and frequency of delivery is a function of plant size and location. Generally, the larger the facility, the more numerous and voluminous the creosote deliveries will be. Increased frequency and quantity means increased potential for emissions. Transfer of the preservative, whether from rail car or tanker, is normally accomplished using a closed piping system. In such a system, the greatest chance for fugitive emissions is at the origin, where creosote is leaving the tanker or rail car, and at the end of the transfer, where creosote is entering the storage vessel (Wallingford and Que Hee, 1985; Andersson et al., 1983).

The storage of creosote-impregnated lumber products at a treatment facility has been identified as the most significant POM emission source of the entire operation. The evaporative fugitive emissions from product storage are dependent on both the treatment process (primarily the preservative solution constituency) and the flux through the storage cycle. As would be expected, fresh product POM emissions are greater than aged product emissions (Koppers Ind., 1990). If treated products are stored in a building, emissions of this type would be largely confined and atmospheric emissions significantly reduced (Wallingford et al., 1985; Andersson et al., 1983).

According to EPA, only a small percentage of creosote wood treatment facilities have air pollution control systems. Most facilities use vapor condensers for product recovery from treatment cylinders. These condensers also serve to significantly reduce the vaporous POM concentrations in cylinder fugitive and vacuum pump gases. Seven or eight U.S. facilities are currently using wet scrubbers to control emissions from treatment vessels and vacuum pumps. One facility is operating a fume incinerator, which was tested for total hydrocarbon by EPA in 1993. Hydrocarbon emissions were non-detectable at the fume incinerator outlet. Biological treatment technologies are currently being marketed to the wood treatment industry for both water treatment and post-scrubber air polishing (Crumpler Telecon, 1994).

Emission Factors

Emission factors for three processes in the creosote wood treatment source category were derived from two test reports conducted at a single facility. The emission factors represent the following processes/process groupings: (1) the creosote treatment process with associated chemical handling and treatment process fugitives; (2) the diluent treatment process with associated chemical handling and treatment process fugitives; and (3) the treated wood product storage piles.

PAH emission factors for the creosote wood treatment process and associated process fugitives are presented in Table 4.12.2-1. The emission factors represent emissions from the creosote working tank vent, the treatment cylinder vacuum exhaust, the cylinder fill vent, the cylinder sump, rail tank car unloading, the oil water separator, and cylinder piping. The reported emissions data used in emission factor development were based on a combination of point source stack sampling, emission factors based on liquid sampling, and mass balance calculations.

TABLE 4.12.2-1. PAH EMISSION FACTORS FOR CREOSOTE WOOD TREATMENT

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ft^3 (kg/m^3)[b]	Emission Factor Rating[c]
3-07-005-01	Treatment Cylinder and Process Fugitives	Vapor Condenser	Acenaphthylene	6.13E-04 (9.83E-03)	U
			Fluorene	1.67E-04 (2.67E-03)	U
			Naphthalene	2.20E-03 (3.52E-02)	U
			Phenanthrene	1.14E-04 (1.83E-03)	U
			2-Methylnaphthalene	2.58E-03 (4.14E-02)	U

[a] Point sources: Creosote working tank vent, cylinder vacuum exhaust, and cylinder fill vent; Fugitive sources: Rail tank car unloading, cylinder sump, cylinder unloading, oil/water separator, and cylinder piping.

[b] Emission factors are in lb (kg) of pollutant emitted per ft^3 (m^3) of treated wood produced and are based on stack sampling data, liquid sampling data/emission factors, and material balance.

[c] Factor was assigned a U rating because factors were developed from mass balance data that did not have sufficient supporting documentation to determine a valid rating.

Source: Ebasco, 1989; Koppers Ind., 1990.

PAH emission factors for the diluent wood treatment process and associated process fugitives are presented in Table 4.12.2-2. The diluent process involved wood treatment using creosote mixed with No. 6 fuel oil. The emission factors represent emissions from the diluent working tank vent, the treatment cylinder vacuum exhaust, the cylinder fill vent, the cylinder sump, rail tank car unloading, the oil water separator, and cylinder piping. The reported emissions data used in emission factor development were based on a combination of point source stack sampling, emission factors based on liquid sampling, and mass balance calculations.

Fugitive emissions from both treatment process ancillary operations (i.e., other than direct treatment process emissions) were germane to both the creosote and diluent processes. This category of general fugitive emissions included such processes as wastewater treatment, cylinder sumps, chemical unloading, and piping fugitive emissions from piping common to both treatment operations.

Specific PAH emissions data for both the creosote and diluent treatment process were available for the five most prevalent species emitted. Additional categories identified in the reported test data were titled “additional PAHs detected” and “PAHs below detection limits in gas stream.” However, the magnitude of these grouped emissions for both processes was significantly lower than the lowest-emitting PAH species reported.

PAH emission factors for creosote-treated wood product storage piles are presented in Table 4.12.2-3. Testing was conducted at a wood treatment facility under enclosed conditions with induced air flow. Treated timbers of various ages, from 1 to 30 days post-treatment, were tested to determine an average emission factor per unit stored with an assumed flux of material to and from the storage yard. The total magnitude of PAH emissions from product storage has been reported at approximately 1.6 percent of the total amount of PAH compounds found in the process chemical used per year. This compares to 2.0 percent emitted from all treatment and storage operations combined (Ebasco, 1989).

TABLE 4.12.2-2. PAH EMISSION FACTORS FOR DILUENT WOOD TREATMENT

SCC Number	Emission Source[a]	Control Device	Pollutant	Average Emission Factor in lb/ft^3 (kg/m^3)[b]	Emission Factor Rating[c]
3-07-005-01	Treatment Cylinder and Process Fugitives	Vapor Condenser	Acenaphthene	8.08E-05 (1.29E-03)	U
			Fluorene	3.72E-05 (5.96E-04)	U
			Naphthalene	6.28E-04 (1.01E-02)	U
			Phenanthrene	4.11E-05 (6.58E-04)	U
			2-Methylnaphthalene	4.91E-04 (7.86E-03)	U

[a] Point sources: Creosote working tank vent, cylinder vacuum exhaust, and cylinder fill vent; Fugitive sources: Rail tank car unloading, cylinder sump, cylinder unloading, oil/water separator, and cylinder piping.

[b] Emission factors are in lb (kg) of pollutant emitted per ft^3 (m^3) of treated wood produced and are based on stack sampling data, liquid sampling data/emission factors, and material balance.

[c] Factor was assigned a U rating because factors were developed from mass balance data that did not have sufficient supporting documentation to determine a valid rating.

Source: Ebasco, 1989; Koppers Ind., 1990.

TABLE 4.12.2-3. PAH EMISSION FACTORS FOR CREOSOTE/DILUENT TREATED WOOD STORAGE

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ft^3 (kg/m^3)^a	Emission Factor Rating
3-07-005-01	Treated Wood Storage Pile	None	Benzo(a)pyrene	1.23E-08 (1.96E-07)	E
			Benzo(b)fluoranthene	1.35E-06 (2.16E-05)	E
			Benzo(k)fluoranthene	1.12E-06 (1.79E-05)	E
			Chrysene	4.78E-08 (7.66E-07)	E
			Dibenz(a,h)anthracene	1.69E-12 (2.70E-11)	E
			Indeno(1,2,3-cd)pyrene	5.90E-12 (9.46E-11)	E
			Acenaphthene	0.0117 (0.187)	E
			Acenaphthylene	4.18E-04 (6.69E-03)	E
			Anthracene	4.03E-04 (6.46E-03)	E
			Benzo(ghi)perylene	5.22E-12 (8.36E-11)	E
			Fluoranthene	4.13E-04 (6.61E-03)	E
			Fluorene	6.66E-03 (1.07E-01)	E

(continued)

TABLE 4.12.2-3. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ft^3 (kg/m^3)[a]	Emission Factor Rating
3-07-005-01 (continued)	Treated Wood Storage Pile (continued)	None	Naphthalene	0.0222 (0.355)	E
			Phenanthrene	8.58E-03 (0.137)	E
			Pyrene	7.80E-05 (1.25E-03)	E

[a] Emission factors are in lb (kg) of pollutant emitted per ft^3 (m^3) of treated wood stored and are based on pilot stack sampling data.

Source: Koppers Ind., 1990.

Source Locations

Creosote wood treatment plants are located across the country, but they are predominantly found in the Southeast. Information compiled by the American Wood Preservers Association and the American Wood Preservers Institute indicates that there are roughly 83 creosote pressure treatment plants nationwide (Micklewright, 1990). A list identifying these facilities is given in Table 4.12.2-4.

TABLE 4.12.2-4. LIST OF CREOSOTE WOOD PRESSURE TREATMENT PLANTS IN THE UNITED STATES IN 1989

Company	Location
Brown Wood Preserving Company, Inc.	Northport, AL
Cahuba Pressure Treated Forest Products	Brierfield, AL
Huxford Pole and Timber Company, Inc.	Huxford, AL
I. R. Miller Mill Company, Inc.	Brewton, AL
Koppers Company, Inc.	Montgomery, AL
Seaman Timber Company	Montevallo, AL
Stallworth Timber Company	Beatrice, AL
Arizona Pacific Wood Preserving, Inc.	Elroy, AZ
Koppers Company, Inc.	North Little Rock, AR
Thompson Industries, Inc.	Russellville, AR
J. H. Baxter and Company	Weed, CA
Koppers Company, Inc.	Oroville, CA
McCormick & Baxter Creosoting Company	Stockton, CA
Pacific Wood Preserving of Bakersfield	Bakersfield, CA
San Diego Wood Preserving	National City, CA
Koppers Company, Inc.	Denver, CO
Perma Treat Corporation	Durham, CT
Koppers Company, Inc.	Gainesville, FL
Atlantic Wood Industries, Inc.	Port Wentworth, GA
B & M Wood Products, Inc.	Manor, GA
Baxley Creosoting Company, Inc.	Baxley, GA
Brunswick Wood Preserving Company, Inc.	Brunswick, GA
Glennville Wood Preserving Company	Glennville, GA
Manor Timber Company, Inc.	Manor, GA
Union Timber Corporation	Homerville, GA
Kerr-McGee Chemical Corporation	Madison, IL
Koppers Company, Inc.	Carbondale, IL
Koppers Company, Inc.	Galesburg, IL

(continued)

TABLE 4.12.2-4. (Continued)

Company	Location
Hoosier Treating Company	Gosport, IN
Kerr-McGee Chemical Corporation, FPD	Indianapolis, IN
Western Tar Products Corporation	Terre Haute, IN
Easterday Tie and Timber Company	Mayfield, KY
Koppers Company, Inc.	Guthrie, KY
L. L. Benton Creosoting Works	Benton, LA
Colfax Creosoting Company	Pinesville, LA
Dura-Wood Treating Company	Alexandria, LA
International Paper Company, IWP Division	DeRidder, LA
Madisonville Wood Preserving Company	Madisonville, LA
Superior Tie and Timber	Vivian, LA
Eastern Maryland Wood Treating Company	Federalsburg, MD
American Wood	Richton, MS
Brookhaven Wood Preserving Company	Brookhaven, MS
Kerr-McGee Chemical Corporation	Columbus, MS
Koppers Company, Inc.	Grenada, MS
Pearl River Wood Preserving Corporation	Picayune, MS
Timco, Inc.	Wiggins, MS
Wood Treating, Inc.	Picayune, MS
Kerr-McGee Chemical Corporation	Springfield, MO
Atlantic Wood Industries, Inc.	Hainesport, NJ
General Timber, Inc.	Sanford, NC
General Wood Preserving Company, Inc.	Leland, NC
Holcomb Creosote Company	Yadkinville, NC
Julian Lumber Company	Antlers, OK
Mixon Brothers Wood Preserving Company	Idabel, OK
J. H. Baxter and Company	Eugene, OR
Kerr-McGee Chemical Corporation	The Dalles, OR
McCormick and Baxter Creosoting Company	Portland, OR

(continued)

TABLE 4.12.2-4. (Continued)

Company	Location
Taylor Lumber & Treating, Inc.	Sheridan, OR
Burke-Parsons-Bowlby Corporation	DuBois, PA
H.P. McGinley, Inc.	McAlisterville, PA
Kerr-McGee Chemical Corporation	Avoca, PA
Koppers Company, Inc.	Montgomery, PA
Mellot Wood Preserving Company, Inc.	Needmore, PA
Koppers Company, Inc.	Florence, SC
Wheeler Lumber Operations	Whitewood, SD
Conroe Creosoting Company	Conroe, TX
Garland Creosoting Company	Longview, TX
Hart Creosoting Company	Jasper, TX
Hicks Post Company	Alto, TX
Kerr-McGee Chemical Corporation	Texarkana, TX
Lufkin Creosoting Company, Inc.	Lufkin, TX
W. J. Smith Wood Preserving Company	Denison, TX
AT&SF Ry Company	Somerville, TX
Texas Electric Cooperative, Inc.	Jasper, TX
Atlantic Wood Industries, Inc.	Portsmouth, VA
Burke-Parsons-Bowlby Corporation	Goshen, VA
Koppers Company, Inc.	Salem, VA
Wood Preservers, Inc.	Warsaw, VA
J. H. Baxter and Company	Arlington, WA
McFarland Cascade	Tacoma, WA
Pacific Wood Treating Corporation	Ridgefield, WA
Wyckoff Company	Seattle, WA
Acme Wood Preserving, Inc.	Princeton, WV
Appalachian Timber Services, Inc.	Sutton, WV
Burke-Parsons-Bowlby Corporation	Spencer, WV

(continued)

TABLE 4.12.2-4. (Continued)

Company	Location
Koppers Company, Inc.	Green Spring, WV
Koppers Company, Inc.	Superior, WI
Webster Wood Preserving Company	Bangor, WI

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 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: Micklewright, 1990.

SECTION 4.12.2 REFERENCES

Andersson, K. et al. “Sampling and Analysis of Particulate and Gaseous Polycyclic Aromatic Hydrocarbons from Coal Tar Sources in the Working Environment.” Chemosphere. 12(2):197-207. 1983.

Crumpler, E., U.S. Environmental Protection Agency, telephone conversation with P.A. Keller, Radian Corporation. “Wood Treatment MACT Development Preliminary Data.” June 16, 1994.

Ebasco Services, Inc. Final Emission Test Report, Emission Testing Program, Koppers Superfund Site, Oroville, California. EPA Contract No. 68-01-7250. pp. 1.1-1.5, 3.1-3.13, and 6.1-6.39. December 1989.

Koppers Industries, Inc. “AB2588 Emission Test Program.” Oroville, California. 7 pp. October 8-12, 1990.

Micklewright, J.T. A List of Wood Preserving Plants in the United States including Address, Location, and Number of Pressure Cylinders. American Wood Preservers Institute, Vienna, Virginia. 53 pp. 1990.

U.S. Department of Agriculture. The Biologic and Economic Assessment of Pentachlorophenol, Inorganic Arsenical, and Creosote - Volume I: Wood Preservatives. U.S. Department of Agriculture, Washington, DC. USDA Technical Bulletin No. 1658-1. November 1980.

U.S. Environmental Protection Agency. Title III, Section 313: Release Reporting Guidance, Estimating Chemical Releases from Wood Preserving Operations. Office of Pesticides and Toxic Substances, Washington, DC. EPA-560/4-88-004p. 11 pp. February 1988.

Vaught, C.C., and R.L. Nicholson. Evaluation of Emission Sources from Creosote Wood Treatment Operations. Prepared for U.S. Environmental Protection Agency, Control Technology Center, Research Triangle, Park, North Carolina. EPA-450/3-89-028. 33 pp. June 1989.

Wallingford, K.M., and S.S. Que Hee. “Occupational Exposure to Benzo(e)pyrene.” In: Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods, and Metabolism, Proceedings of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1983. M. Cooke and A.J. Dennis, eds. Battelle Press, Columbus, Ohio. 1985.

Ware, P., Vulcan Chemicals, Letter to D. Beauregard, U.S. Environmental Protection Agency. January 9, 1996.

4.12.3 Carbon Regeneration

Process Description

Activated carbon is used primarily for adsorbing pollutants from water or air (e.g., in industrial or municipal wastewater treatment plants). Because of increasing environmental awareness and tighter regulations, the demand for activated carbon is increasing. Used carbon can be regenerated (reactivated) by essentially the same process used for the original activation. The regeneration process creates the potential for POM formation and emissions.

In the regeneration process, organics adsorbed on the carbon during use are burned off by placing the spent carbon in continuous internally or externally fired rotary retorts or, most commonly, in multiple-hearth furnaces. Figure 4.12.3-1 shows a cross-section of a typical multiple-hearth furnace. In this type of furnace, the charge (carbon) is stirred and moved from one hearth to the next-lower hearth by rotating rabble arms. For smaller-scale regeneration operations, fluidized-bed and infrared furnaces can be used. The various furnace types used for carbon regeneration and the approximate number of furnaces of each type are shown in Table 4.12.3-1.

In a typical regeneration process, spent carbon in a water slurry form is fed from a surge tank to a dewatering screw, which feeds the spent carbon to the top of the furnace. In the furnace, the spent carbon is dried and the organics on the carbon are volatilized and burned as the carbon is regenerated. The regenerated carbon drops from the bottom hearth of the furnace to a quench tank and is stored as a slurry (U.S. EPA, 1987). A flow diagram of the carbon regeneration process is shown in Figure 4.12.3-2.

A hot gas, such as steam or CO_2, is introduced into the furnace at temperatures of approximately 1,498 to 1,858°F (800 to 1,000°C), although some excess oxygen is typically present throughout the furnace (Byers, 1991). The regeneration process is exothermic, using the heating value of the volatile carbon plus heat supplied from supplemental fuel (e.g., natural gas).

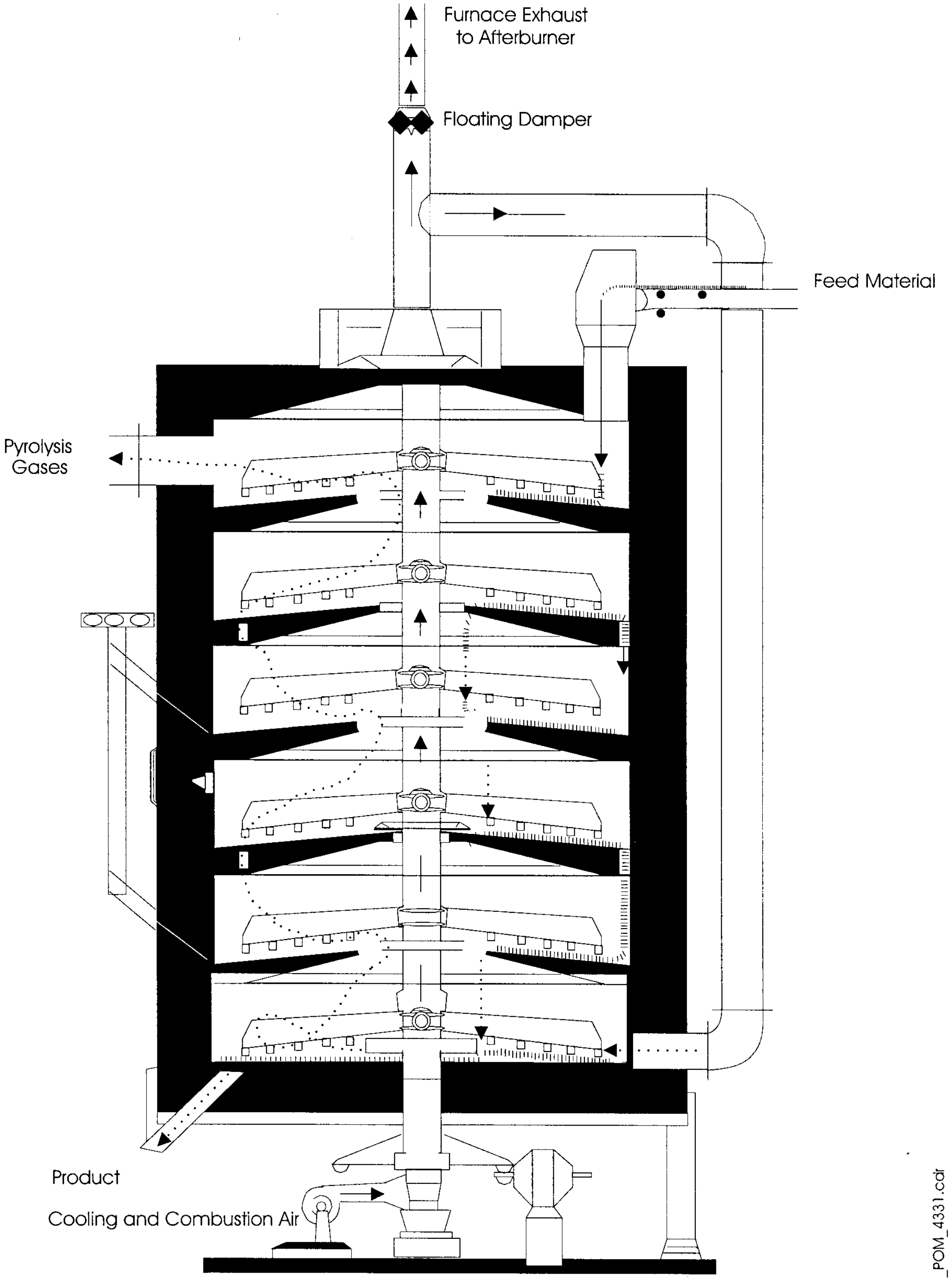


Figure 4.12.3-1. Cross-section of a Typical Multiple-hearth Furnace

Source: U.S. EPA, 1997.

TABLE 4.12.3-1. TYPES OF EQUIPMENT USED FOR ACTIVATED CARBON REGENERATION

Furnace Type	Approximate No. of Units in United States
Multiple-hearth	<100
Fluidized-bed	<20
Indirect-fired rotary kiln	>50
Direct-fired rotary kiln	<30
Vertical-tube type	<30
Infrared-horizontal	<5
Infrared-vertical	4

Source: Shuliger and Knapil, 1990.

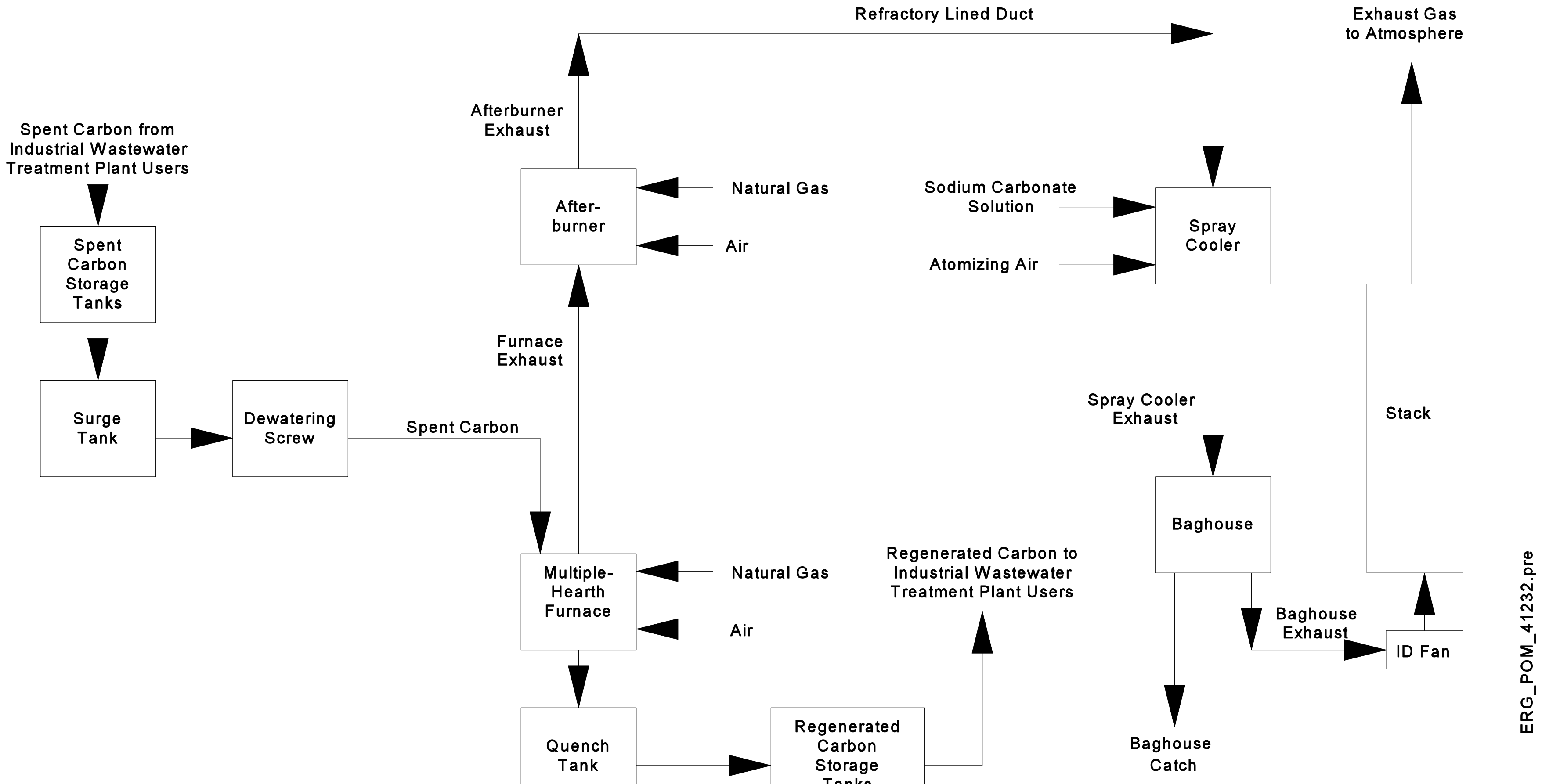


Figure 4.12.3-2. Process Flow Diagram of Carbon Regeneration Process

Source: U.S. EPA, 1993.

A typical furnace may fire an average of 459,089 ft^3/day (13,000 m^3/day) of natural gas (U.S. EPA, 1987).

Typical industrial carbon regeneration plants may process up to 109,127 lb/day (49,500 kg/day) of spent carbon from numerous industrial or municipal facilities that use activated carbon for wastewater treatment (U.S. EPA, 1987). Regeneration plants may operate 24 hours per day, 7 days per week for much of the year, with periodic shutdowns for furnace maintenance.

Emissions from carbon activation and regeneration processes contain a number of toxic air pollutants. Regeneration has an even greater potential for producing toxic emissions because the carbon has often been used to adsorb compounds classified as toxic air pollutants (Byers, 1991).

The potential for POM formation exists in the high-temperature, low-oxygen environment of the regeneration furnace. POM compounds are more likely formed from the adsorbed organics on the spent carbon rather than from impurities in the virgin carbon.

The primary point source of emissions from the carbon regeneration process is the furnace exhaust. These emissions are typically controlled by afterburners followed by water scrubbers (U.S. EPA, 1987). The afterburner may consist of a short vertical section with natural gas-fired burners and a long horizontal section of refractory-lined duct with no burners. Afterburner combustion temperatures of 1,822°F (980°C) or greater and residence times in excess of 2 seconds are typical (Byers, 1991). Temperatures greater than 1,625°F (871°C) and residence times longer than 0.5 seconds are recommended (U.S. EPA, 1987). There are no available data on the destruction and removal efficiency (DRE) for an afterburner control system in this application. However, the conditions and configuration are similar to those used for controlling hazardous waste incinerator emissions, where DREs of 99.99 percent are typical (Byers, 1991).

Exhaust gases from the afterburner can be cooled by an alkaline (e.g., sodium carbonate) spray cooler in which an atomized dilute alkaline solution is mixed with the exhaust gas. The alkaline medium neutralizes acid gases to permit compliance with regulatory emission limits (Byers, 1991). From the spray cooler, the exhaust gases may enter centrifugal or fabric filter (baghouse) collectors, which are used to control particulate and reaction products from upstream components. Collection efficiencies of 65 percent for centrifugal collection and 99 percent for fabric filtration have been reported (Byers, 1991). The collected particulate is ultimately disposed of in a landfill.

Emission Factors

PAH concentrations and mass emission rates from a municipal wastewater treatment plant carbon reactivation furnace were quantified in one test report (BTC Env., 1991). Insufficient data were available in the report to develop PAH emission factors. The unit tested was a reactivation furnace of unspecified design used to reactivate carbon for tertiary wastewater treatment. The furnace was fired with natural gas, using steam from a co-located natural gas-fired boiler. The unit was equipped with an afterburner and a scrubber. The controlled exhaust gases from the furnace were sampled using CARB Method 429 and analyzed for specific PAHs. The following PAHs were detected in one or more of the three sampling runs: benz(a)anthracene, benzo(b&k)fluoranthene, chrysene, acenaphthalene, anthracene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene.

Source Locations

Activated carbon is used primarily to adsorb organics from water at industrial or municipal wastewater treatment plants. Carbon regeneration may be performed at the site where the carbon was used (on-site regeneration) or at a commercial regeneration facility that processes spent carbon from multiple industries. Because of the large number of potential individual locations of regeneration facilities, listing specific sites is not feasible here.

SECTION 4.12.3 REFERENCES

BTC Environmental, Inc. AB-2588 Toxic Emission Testing, Orange County Water District, 10500 Ellis Avenue, Fountain Valley, California. pp. 1-5. April 29 1991 to May 8, 1991.

Byers, W.D. Charcoal/Activated Carbon, Air Pollution Engineering Manual. Buonicore, A.J., and W.J. Davis, eds. Van Nostrand Reinhold, New York, New York. pp. 413-416. 1991.

Schuliger, W.G., and L.G. Knapil. “Reactivation Systems.” In: Sunday Seminar, American Water Works Association Annual Conference, June 1990.

U.S. Environmental Protection Agency. Locating and Estimation Air Emissions from Sources of Dioxins and Furans. Prepared for U.S. Environmental Protection Agency, Emission Inventory Branch, Research Triangle Park, North Carolina. EPA-454/R-97-003. 1997.

U.S. Environmental Protection Agency. National Dioxin Study, Tier 4 -Combustion Sources, Final Test Report - Site 9, Carbon Regeneration Furnace CRF-A. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/4-84-014r. pp. 3-1 to 3-2. April 1987.

4.12.4 Cigarette Smoke

Process Description

The smoke produced from burning cigarettes and other tobacco products has been intensively researched in the last three decades. Previously, the concern over health risks from cigarette smoke was focused on the smoker. Recently the impact of environmental tobacco smoke (ETS), also known as passive smoke or “second-hand” smoke, on non-smokers has also been investigated. The preliminary indications are that ETS presents a health problem for non-smokers that approaches the impact of cigarette smoke on the smoker (National Academy of Sciences, 1989).

The impacts of ETS have primarily been viewed as a component of the issue of indoor air quality. However, ETS represents one of the many small sources contributing POM to the outdoor urban atmosphere. One estimate is that cigarette smoke accounted for about 2.7 percent of the fine organic aerosol emission in the Los Angeles area atmosphere in 1982 (Rogge et al., 1994). This contribution can be expected to grow as smoking is increasingly restricted to the outdoors at many facilities and workplaces.

Emission Factors

A recent study was conducted to trace cigarette smoke PM in outdoor ambient air (Rogge et al., 1994). Tracer compounds were identified in cigarette smoke that demonstrated the following necessary features: the compound is fairly stable in the atmosphere; the compound is present in a known ratio to the cigarette smoke PM mass concentration; and the compound is distinguishable from PM from other anthropogenic or biogenic sources. The class of PAH compounds met all three of these conditions and were considered suitable tracer compounds for ETS.

Cigarette smoke was sampled and analyzed for PAH and other suitable tracer compounds. The exhaled mainstream smoke and sidestream smoke (the smoke from the cigarette that is not exhaled) from human smokers was sampled in a specially designed, vertically oriented, dilution tunnel, which allowed sufficient time for condensible organic compounds emitted in the vapor phase to equilibrate with smoke particles prior to sampling. Hence, only the PM in the smoke was collected, and the PAH adsorbed onto the PM was analyzed. This test design most closely approximates the conditions and the form of the PAH that would be expected in the ambient air. Based on these tests, emission factors for PAH in cigarette smoke that are released to the environment are reported in Table 4.12.4-1.

Source Location

Because cigarette smoke is emitted from area sources, the location of the emissions need not be specified.

TABLE 4.12.4-1. PAH EMISSION FACTORS FOR CIGARETTE SMOKE

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/cigarette (kg/cigarette)[a]	Emission Factor Rating
A-28-10-XXX-XXX	Cigarette	Uncontrolled	Benz(a)anthracene	6.0E-10 (2.7E-10)	A
			Chrysene/Triphenylene	1.5E-09 (6.7E-10)	A
			Anthracene	1.7E-09 (7.6E-10)	A
			Fluoranthene	2.1E-09 (9.5E-10)	A
			Phenanthrene	5.8E-09 (2.6E-09)	A
			Pyrene	2.2E-09 (1.0E-09)	A
			2-Phenylnaphthalene	8.2E-10 (3.7E-10)	A
			Benzacenaphthylene	6.6E-10 (3.0E-10)	A
			Benzo(a)fluorene/ Benzo(b)fluorene	1.2E-09 (5.4E-10)	A
			Dimethylfluoranthenes/ Dimethylpyrenes	1.2E-09 (5.5E-10)	A
			Methylbenz(a)anthracenes/ Methylchrysenes/ Methyltriphenylenes	1.5E-09 (6.9E-10)	A

(continued)

TABLE 4.12.4-1. (Continued)

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/cigarette (kg/cigarette)[a]	Emission Factor Rating
A-28-10-XXX-XXX (continued)	Cigarette (continued)	Uncontrolled (continued)	Methylfluoranthenes/ Methylpyrenes	2.9E-09 (1.3E-09)	A
			Methylphenanthrenes/ Methylanthracenes	7.7E-09 (3.5E-09)	A

[a] Emission factors in lb (kg) per cigarette smoked.

Source: Rogge et al., 1994.

SECTION 4.12.4 REFERENCES

National Academy of Sciences. Environmental Tobacco Smoke: Measuring Exposure and Assessing Health Effects. National Academy Press, Washington, DC. 1989.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, and G.R. Cass. “Sources of Fine Organic Aerosol: 6. Cigarette Smoke in the Urban Atmosphere.” Environmental Science and Technology, Volume 28, No. 7, pp. 1375-1388. 1994.

4.12.5 Wood Charcoal Production

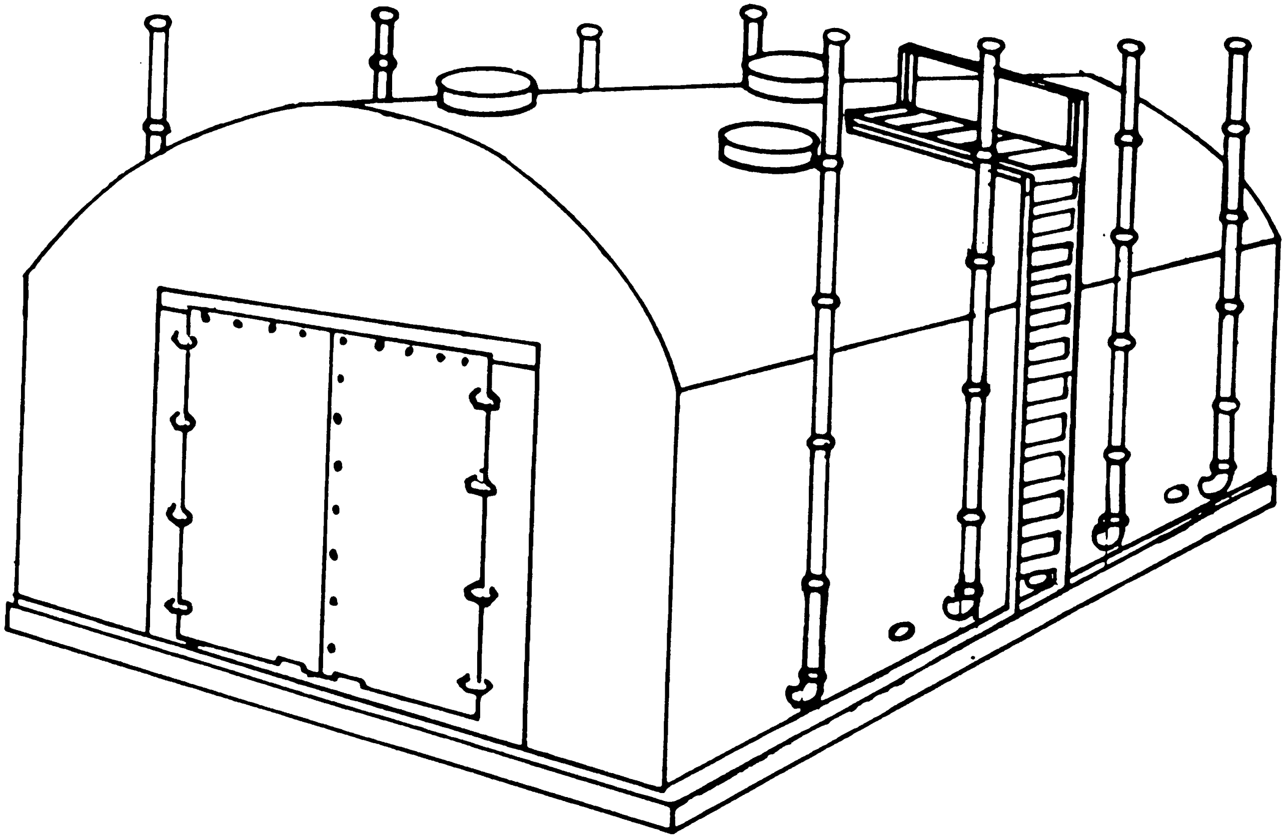
Process Description

Charcoal, which is primarily used for outdoor cooking, is manufactured by the pyrolysis of carbonaceous raw materials, mainly medium to dense hardwoods such as beech, birch, maple, hickory, and oak. Softwoods, sawdust, nutshells, fruit pits, and vegetable wastes are also used in the pyrolysis process. The high-temperature (842 to 950°F [450 to 510°C]) pyrolysis of wood materials is a potential means of generating POM emissions (Kelly, 1983).

Hardwood charcoal is manufactured by a four-step pyrolysis process. Heat is applied to the wood and as the temperature rises to 212°F (100°C), water and highly volatile hydrocarbons are distilled off. The wood temperature remains at approximately 100°C until the moisture content of the wood has been removed. At this time the volume of distillate production declines and the wood temperature begins to climb. During the next stage, the wood temperature rises with heat input to approximately 527°F (275°C) and hydrocarbon distillate yield increases. As the third stage begins (at approximately 275°C), external application of heat is no longer required because the carbonization reactions become exothermic. During this stage, the wood temperature rises to 662°F (350°C), and the bulk of hydrocarbon distillates are produced. At approximately 350°C, exothermic pyrolysis ends, and during the final stage, heat is again applied, raising the wood temperature to 752 to 932°F (400 to 500°C) to remove more of the less volatile, materials from the product charcoal.

Currently, there are two predominant vessel types used to manufacture wood charcoal: the Missouri-type batch kiln and the continuous Herreshoff furnace.

Missouri-type Batch Kiln--The batch process and kiln account for about 45 percent of national wood charcoal production. The Missouri-type kiln, shown in Figure 4.12.5-1, is typically constructed of concrete (Moscowitz, 1978) and normally processes about 45 to 50 cords of wood in a 10- to 25-day cycle. A typical cycle may be structured as follows:



ERG_POM_412_51.ds4

Figure 4.12.5-1. Missouri-type Charcoal Kiln

Source: Moscowitz, 1978.

- 1 to 2 days: load wood;
- 5 to 8 days: pyrolysis;
- 10 to 14 days: cool; and
- 1 to 2 days: unload charcoal.

After the wood is manually loaded into the kiln, a fire is started, usually at the bottom center of the kiln, by igniting easily combustible materials placed at this point during the loading. Ignition patterns are generally similar for all types of kilns. During ignition, a large amount of air is necessary for the rapid combustion of the starting fuels to ensure the heat level needed for pyrolysis. This air is supplied through groundline ports in the kiln side walls or through temporary openings under the kiln door. In some cases, the kiln doors remain open until the burn is adequately started. Auxiliary ceiling ports in some kilns serve as temporary stacks and aid ignition by causing greater amounts of air to be drawn into the kiln through the air ports. They also aid in removal of smoke from the kiln (Moscowitz, 1978).

Satisfactory carbonization depends primarily on the maintenance of proper burning conditions in the pyrolysis zone. Sufficient heat must be generated first to dry the wood and then to maintain the temperatures necessary for efficient carbonization. At the same time, the burning must be limited so that only sufficient heat is present to produce good charcoal. Temperature control is attained by varying the size of the air port openings providing air for combustion of wood volatiles (Moscowitz, 1978).

For the production of good-quality charcoal, kiln temperatures from about 842 to 950°F (450 to 510°C) are required. Prolonged higher temperatures will reduce the yield of charcoal without necessarily upgrading it for recreational use. On the other hand, if pyrolysis temperatures remain low, the charcoal may be too smoky for domestic use, and larger than normal amounts of brands (partially charred wood) will be produced (Moscowitz, 1978).

When pyrolysis has been completed, all air ports are sealed for the start of the cooling cycle. To prevent the development of gas pressure in the kiln, after the ports are sealed, the stacks remain open until smoking has practically stopped. Stacks can usually be sealed within 1 to 2 hours after the air ports are closed. The kiln is allowed to cool for about 10 to 14 days before removing the charcoal. Yields of approximately 25 percent are achieved (Moscowitz, 1978).

The required pyrolysis time and resultant POM emissions from a Missouri-type batch kiln vary with kiln capacity, operational practices, wood type, and wood moisture content. Process reaction gases containing POM are exhausted from the kiln in stacks that run along the side walls of the vessel (Kelly, 1983; Moscowitz, 1978). The charcoal product of a batch kiln process is either sold directly or made into briquettes for sale.

Herreshoff Multiple-Hearth Furnace--Continuous charcoal production is accomplished in Herreshoff multiple-hearth furnaces. The use of continuous multiple-hearth units for charcoal production has increased because of the following advantages of the units:

- Lower labor requirements than kiln operations, where manual loading and unloading is needed. Only one man per shift is required for continuous facilities.
- Consistent yield and quality charcoal with easy control of product volatile and fixed carbon content.
- Feed of multiple forms of wood waste.
- Offgases easily collected for further processing.

The typical feedstock capacity of continuous wood charcoal furnaces is 2.75 tons/hr (2.5 Mg/hr).

The operating principles of the Herreshoff furnace (Figure 4.12.5-2) are relatively simple. Passing up through the center of the furnace is a shaft to which are attached 2 to 4 rabble arms for each hearth. As the shaft turns, the hogged wood material resting on the hearth floors is continually agitated, exposing fresh material to the hot gases being evolved. A further function of the rabble arms is to move material through the furnace. On alternate hearths, the teeth

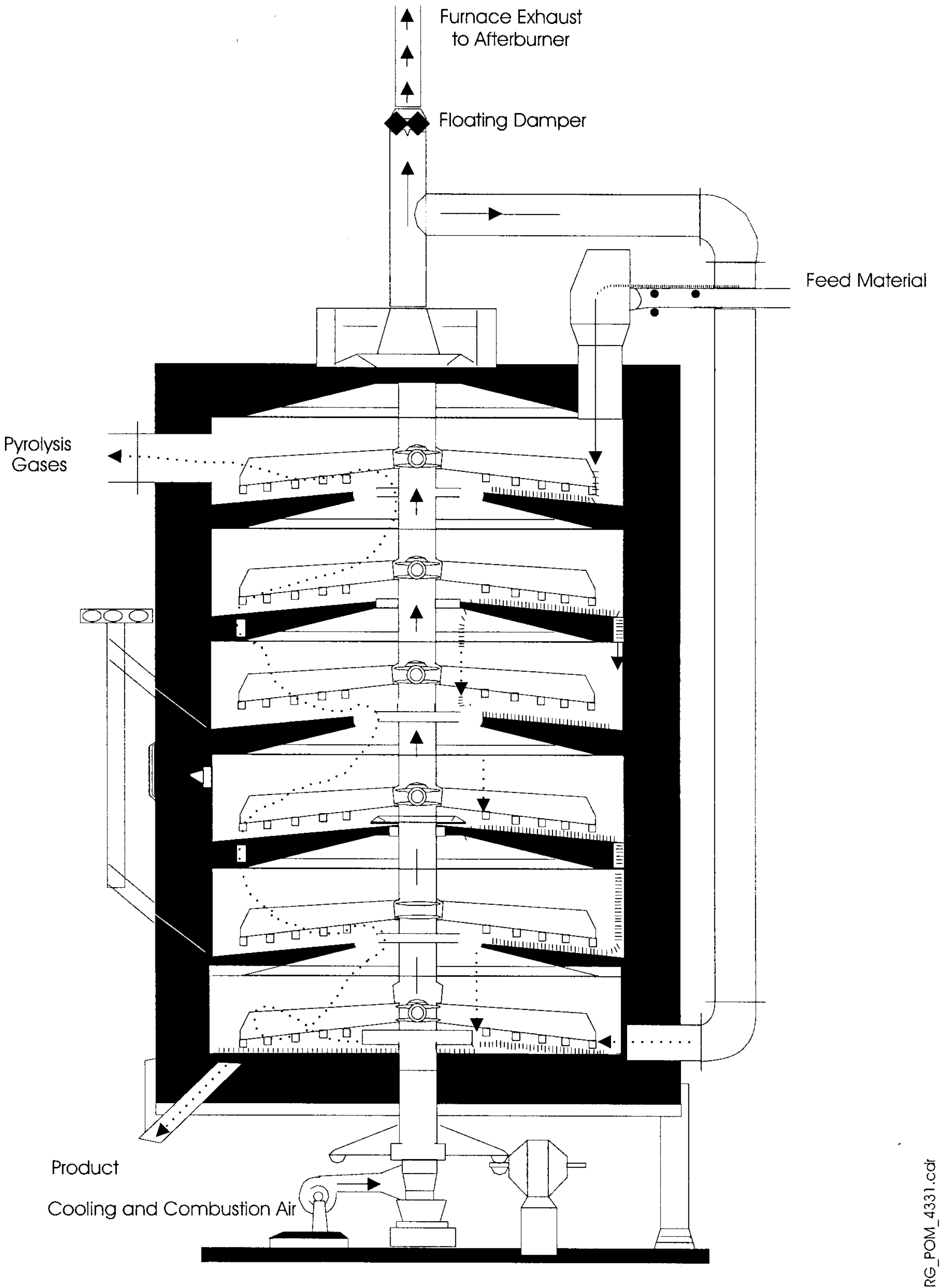


Figure 4.12.5-2. Multiple-Hearth Furnace for Charcoal Production

Source: Moscowitz, 1978.

are canted to spiral the material from the shaft toward the outside wall of the furnace or from the outside wall toward the center shaft. Around the center shaft is an annular space through which material drops on alternate hearths, while on the remaining hearths material drops through holes in the outer periphery of the hearth floor. In this way, material fed at the top of the furnace moves alternately across the hearths at increasing temperatures until it discharges from the floor of the bottom hearth.

Charcoal exiting the furnace is cooled by water sprays and water jacketing on a cooler. These sprays are controlled automatically by a temperature regulator set for a given charcoal temperature. As with batch kilns, the charcoal product of continuous kilns is either sold directly or further processed to briquettes for sale (Moscowitz, 1978).

Initial heat for startup is provided by oil- or gas-fired burners mounted in the sides of the hearths. When the appropriate furnace temperature has been attained, the auxiliary fuel ceases, and combustion air is used to ignite the evolving wood gases to maintain furnace temperature. Furnace temperatures range between 896 to 1,202°F (480 to 650°C). Exhaust gases from the charcoal production process are: (1) vented to the atmosphere or to controls through stacks located on top of the furnace, (2) used as a heat source for predrying of feed material and drying of briquettes produced at an adjacent vessel, or (3) burned in a waste heat boiler to produce steam (Kelly, 1983).

A 1978 EPA investigation into wood charcoal production indicated that many of the batch kilns are relatively old and many, particularly smaller kilns, are uncontrolled (Kelly, 1983; Moscowitz, 1978). In general, the control of emissions, including POM, from batch wood charcoal kilns is complicated by the cyclical nature of the process. Throughout the cycle, both emission composition and flow rate change. Direct-fired afterburners for the destruction of hydrocarbons have been suggested as the most feasible control system; however, these devices would require an auxiliary fuel such as natural gas. Economic analyses have indicated that for typical batch kilns, the operation of afterburners for emissions control would cause firms to lose money (Moscowitz, 1978). With the combustion of auxiliary fuel of any type, a potential is also created for additional POM emissions. No information is available on the proportion of batch kilns with afterburner controls or the effect of afterburner use on POM emissions (Kelly, 1983).

Continuous wood charcoal furnaces are predominantly controlled by direct-fired afterburners (Kelly, 1983; Moscowitz, 1978). Auxiliary fuel firing is required in continuous furnace afterburners only during startup or process upsets because of the generally higher heating value of continuous furnace exhaust gases. One facility is using an incinerator to control furnace emissions (Moscowitz, 1978).

Emission Factors

POM emission factor data are available in the literature only for a Missouri-type batch kiln (Kelly, 1983). Five sampling runs were made, and total uncontrolled POM emissions averaged 0.007 lb/ton (3.5 g/Mg) of charcoal produced. Sources and Emissions of Polycyclic Organic Matter indicates that the POM samples from these tests were obtained using a modified Method 5 procedure and sample analysis was performed by gas chromatography (Kelly, 1983). Benz(c)phenanthrene and benzo(a)pyrene were identified as constituents of total POM emissions. Four other POM compounds, dibenz(a,h)anthracene, 3-dimethylcholanthrene, 7,12-dimethylbenz(a)anthracene, and 3,4,5,6-dibenzocarbazole, were specifically analyzed for but were not detected in any of the samples (Kelly, 1983).

The author of Sources and Emissions of Polycyclic Organic Matter notes that the results of the batch kiln emission tests might be of questionable value because of the difficulty of sampling the kiln and “the improvisational sampling techniques” used (Kelly, 1983). No estimate of the accuracy of the test results was provided.

Source Locations

A current list of wood charcoal manufacturing facilities in the United States was not available in statistical references or through the Barbecue Industry Association (BIA) at the time this document was prepared. According to a survey conducted by EPA in 1978, there were over 100 wood charcoal manufacturing facilities in the United States, located in 24 states, primarily Missouri, Arkansas, and several southeastern states (Moscowitz, 1978). Information and contacts for specific member facility locations may be obtained through the BIA (708-369-2404).

SECTION 4.12.5 REFERENCES

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. 5-89 to 5-93. 1983.

Moscowitz, C.W. Source Assessment: Charcoal Manufacturing - State-of- the-Art. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. EPA Report No. 600/2-78-004z. December 1978.

4.12.6 Crematories

Process Description

Crematory incinerators used for human cremation at funeral homes, mortuaries, cemeteries. Crematories are normally of an excess air design, and utilize secondary chamber (afterburner) and primary chamber (ignition) burners fueled by liquified petroleum (LP) gas or natural gas. Burner capacities are generally between 750,000 and 1,500,000 Btu per hour per burner. Later model units have burner modulation capability to regulate chamber temperatures and conserve fuel. Incineration rates range from 100 to 250 lb of remains per hour.

Preheating and a minimum secondary chamber temperature, typically ranging from 1,400°F to 1,800°F, may be requirements. Although not suitable for this batch load type of incinerator, the same requirements are occasionally applied to the primary chamber.

The human remains and cremation container, generally made of cardboard or wood are loaded onto the primary chamber hearth and the primary burner is ignited to begin the cremation process. The remains may be raked at the midpoint of the cremation to uncover unburned material and speed the process. The average cremation takes from 1.5 to 3 hours, after which the incinerator is allowed to cool for a period of at least 30 minutes so that the remains can be swept from the hearth (Springer, 1996).

Emission Factors

Evaluation tests on two propane-fired crematories at a cemetery in California were conducted through a cooperative effort with the Sacramento Metropolitan Air Quality Management District to determine HAP emissions from a crematory (ERC-39). The units were calibrated to operate at a maximum of 1.45 MMBtu per hour. Emissions testing was performed over a two-week period. Thirty-six bodies were cremated during the test period, which equates to two bodies per crematory per day for nine days. The body and cardboard weights and wood process rates for each test per crematory were reported.

Sampling, recovery, and analysis for PAH were performed in accordance with CARB Method 429, which is based on the use of the EPA Modified Method 5 sampling train. Data from stack gas measurements from each of the nine types of tests performed during the evaluation program were tabulated and reported. Emission factors developed from these data are presented in Table 4.12.6-1.

Source Locations

In 1991, there were about 400,500 cremations in more than 1,000 crematories located throughout the United States. Table 4.12.6-2 lists the number of crematories located in each state and the estimated number of cremations performed in each State (CANA, 1992).

TABLE 4.12.6-1. POM EMISSION FACTORS FOR CREMATORIES

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/body (kg/body)[a]	Emission Factor Rating
3-15-021-01	Crematory Stack	Uncontrolled	Acenaphthene	1.11E-07 (5.02E-08)	E
			Acenaphthylene	1.22E-07 (5.54E-08)	E
			Anthracene	3.24E-07 (1.47E-07)	E
			Fluoranthene	2.05E-07 (9.31E-08)	E
			Fluorene	4.17E-07 (1.89E-07)	E
			Naphthalene	6.84E-05 (3.10E-05)	E
			Phenanthrene	2.29E-06 (1.04E-06)	E
			Pyrene	1.61E-07 (7.33E-08)	E

Note: Average weight per body incinerated: body = 141 lb (64 kg); wrapping material = 4 lb (2 kg) cardboard, 3 lb (1.4 kg) wood.

[a] Emission factors in lb (kg) per body incinerated.

Source: ERC-39.

TABLE 4.12.6-2. 1991 U.S. CREMATORY LOCATIONS BY STATE

State	No. of Crematories	No. of Cremations[a]	State	No. of Crematories	No. of Cremations[a]
Alabama	6	1,138	Montana	12	2,502
Alaska	7	790	Nebraska	6	1,139
Arizona	26	10,189	Nevada	11	5,009
Arkansas	13	1,787	New Hampshire	6	1,842
California	141	86,374	New Jersey	16	14,427
Colorado	28	7,432	New Mexico	9	2,134
Connecticut	10	4,260	New York	40	23,946
Delaware	4	1,165	North Carolina	24	4,749
District of Columbia	1	b	North Dakota	1	b
Florida	95	46,775	Ohio	41	12,552
Georgia	14	2,684	Oklahoma	9	1,372
Hawaii	10	3,495	Oregon	34	9,020
Idaho	12	1,949	Pennsylvania	44	12,153
Illinois	44	12,083	Rhode Island	5	1,842
Indiana	21	3,636	South Carolina	10	1,764
Iowa	15	2,241	South Dakota	4	b
Kansas	10	1,559	Tennessee	8	1,712
Kentucky	5	1,192	Texas	36	9,340
Louisiana	6	2,656	Utah	5	769
Maine	4	1,853	Vermont	5	1,570
Maryland	17	5,587	Virginia	25	6,097
Massachusetts	13	8,104	Washington	46	15,673
Michigan	38	13,431	West Virginia	6	582
Minnesota	18	5,662	Wisconsin	29	5,541
Mississippi	4	450	Wyoming	2	b
Missouri	19	4,637			

[a] 1990 data; 1991 data unavailable.
[b] No information available.

Source: CANA, 1992.

SECTION 4.12.6 REFERENCES

Cremation Association of North America (CANA). “Cremation Statistics from Cremationist Journal.” Compiled by CANA. 1992.

ERC-39, California Air Resources Board. Confidential Report.

Springer, J.M., Cremation Association of North America, Letter to D. Beauregard, U.S. Environmental Protection Agency. January 31, 1996.

4.12.7 Gasoline Distribution

Process Description

Gasoline distribution activities represent potential emission sources of one PAH, naphthalene. Because the naphthalene content of gasoline vapors ranges from 0.1 to 1.5 percent, with an average of about 0.5 percent, total hydrocarbon emissions from storage tanks, gasoline transfer, and vehicle fueling will include emissions of naphthalene (U.S. EPA, 1994a). This section lists the sources and factors for naphthalene emissions from gasoline distribution and marketing operations. Also, even though gasoline distribution represents a notable potential source of naphthalene emissions, because only one PAH is associated with gasoline distribution, the discussion has been kept brief in this miscellaneous section. The references may be consulted for a more detailed description of processes and controls.

The gasoline distribution network in the United States operates with the following equipment and facilities:

- Pipelines;
- Tanker ships and barges;
- Tank trucks and railcars;
- Bulk terminals;
- Bulk plants; and
- Service stations.

Gasoline is delivered from the petroleum refinery to bulk terminals by way of pipeline, tanker ship, or barge. Bulk terminals may also receive petroleum products from other terminals. From the bulk terminal, petroleum products (including gasoline) are usually distributed by tank trucks to bulk plants. Both bulk terminals and bulk plants deliver gasoline to private, commercial, and retail customers (i.e., service stations). Daily product throughput at a bulk terminal averages about 250,000 gallons (950,000 liters), in contrast to about 5,000 gallons (19,000 liters) for an average size bulk plant (U.S. EPA, 1994a).

Gasoline vapors and the naphthalene they contain may be emitted at each step in the network. Controls that have been devised include the following:

- Vapor recovery and collection or destruction for marine tank vessel loading and unloading;
- Closed vapor balancing systems for gasoline transfer to and from tank trucks;
- Internal and external floating roof tanks; and
- Control systems on service station equipment and/or on board automobiles and other vehicles (U.S. EPA, 1994a).

A NESHAP for the gasoline distribution source category was promulgated on December 14, 1994. Bulk terminals and pipeline breakout stations are the only kinds of sources in the category that were determined to be major and that are covered by the rule. The gasoline distribution NESHAP establishes MACT for storage vessels, loading racks, leaks from piping and equipment, and vapor leakage from sealed cargo tanks during loading (59 FR 64303). The MACT for the different emission points includes some of the control techniques listed above.

Two sets of standards for marine tank vessel loading and unloading operations were proposed on May 13, 1994 (59 FR 25004). One set of standards was proposed under Section 183(f) of the CAA and requires the application of reasonably available control technology (RACT) for VOC and HAP. The other set of standards is the proposed NESHAP for the source category, which establishes MACT for emissions that are directly caused by the loading and unloading of bulk liquids at points where marine terminal equipment is connected to marine vessel sources. The MACT that was selected is the vapor recovery and reduction technique listed above (59 FR 64303).

Emission Factors

Naphthalene emission factors are presented in Table 4.12.7-1. Most were derived by multiplying the percent fraction of naphthalene reported to be in the gasoline vapors by the VOC emission factors available in EPA's AP-42 document for gasoline distribution and marketing activities (U.S. EPA, 1995).

VOC emission factors for equipment leaks (i.e., emissions from leaking pump seals, valves, connectors loading arm valves, open-ended lines, and other points in the gasoline distribution network) were developed for the gasoline distribution NESHAP, but not in a form appropriate for this document (U.S. EPA, 1994b). Emissions from equipment leaks are not calculated based on gasoline throughput, but rather on the number of valves, connectors, etc., present. If the total number of leaking points at a facility is known, the factors in the reference can be used to estimate emissions. Similarly, emission factors for storage tanks at pipeline breakout stations, and bulk terminals and plants are not provided because there is no single factor that applies. Rather, the equations in EPA's AP-42 document for calculating liquid organic storage emissions can be used with the specific parameters for a particular storage tank, such as diameter, height, etc.

It should be emphasized that the fraction of naphthalene reported in gasoline vapor is an average value; more precise estimates of naphthalene emissions must take into account the specific blend of gasoline and possibly the area of the country and time of the year when the gasoline distribution activity is taking place. The only data available for this source category are for uncontrolled operations. However, this does not indicate that the source category is completely uncontrolled. Controls have been in place for gasoline distribution in the majority of ozone non-attainment areas since 1980. When controls specified by the NESHAP are in full effect, emissions of naphthalene and other hydrocarbons should be decreased substantially.

TABLE 4.12.7-1. NAPHTHALENE EMISSION FACTORS FOR GASOLINE DISTRIBUTION

SCC Number	Emission Source	Control Device	Naphthalene Emission Factor in lb/gal (kg/l)	Emission Factor Rating
Bulk Terminals and Bulk Plants:				
4-06-001-31, -32, -33, -34, -35	Tank Car and Truck Submerged Loading: Normal Service	Uncontrolled	2.5E-05 (3.0E-06)[a]	B
4-06-001-36, -37, -38, -39, -40	Tank Car and Truck Splash Loading: Normal Service	Uncontrolled	6.0E-05 (7.2E-06)[a]	B
4-06-001-41, -42, -43, -44, -45, -46	Tank Car and Truck Submerged and Splash Loading: Vapor Balance Service	Uncontrolled	4.0E-05 (4.9E-06)[a]	B
4-06-001-62	Tank Car and Truck Transit: Loaded, Typical	Uncontrolled	0-5.0E-08 (0-6.0E-09)[a]	[b]
4-06-001-62	Tank Car and Truck Transit: Loaded, Extreme	Uncontrolled	0-4.0E-07 (0-4.8E-08)[a]	[b]
4-06-001-63	Tank Car and Truck Transit: Return With Vapor, Typical	Uncontrolled	0-5.5E-07 (0-6.6E-08)[a]	[b]
4-06-001-63	Tank Car and Truck Transit: Return With Vapor, Extreme	Uncontrolled	0-1.8E-06 (0-2.2E-07)[a]	[b]
Marine Vessel Sources:				
4-06-002-39	Tanker Ballasting	Uncontrolled	4.0E-06 (5.0E-07)[a]	B
4-06-002-40	Ship/Ocean Barge Loading: Typical Situation, Any Cargo	Uncontrolled	9.0E-06 (1.1E-06)[a,c]	D
4-06-002-40	Barge Loading: Typical Situation, Any Cargo	Uncontrolled	1.7E-05 (2.0E-06)[a,c]	D
4-06-002-42, -54, -55, -56, -57	Transit for 1 Week	Uncontrolled	1.4E-05 (1.6E-06)[a]	E

(continued)

TABLE 4.12.7-1. (Continued)

SCC Number	Emission Source	Control Device	Naphthalene Emission Factor in lb/gal (kg/l)	Emission Factor Rating
Service Station Operations:				
4-06-003-01	Underground Tank: Splash filling	Uncontrolled	5.8E-05 (6.9E-06)[d]	B
4-06-003-02	Underground Tank: Submerged Filling	Uncontrolled	3.6E-05 (4.4E-06)[d]	B
4-06-003-06	Underground Tank: Balanced Submerged Filling	Uncontrolled	1.5E-06 (1.6E-07)[d]	B
4-06-003-07	Underground Tank: Breathing and Emptying	Uncontrolled	5.0E-06 (6.0E-07)[d]	D
4-06-006-01	Vehicle Refueling: Displacement Losses	Uncontrolled	5.5E-05 (6.6E-06)[d]	[b]
4-06-006-03	Vehicle Refueling: Displacement Losses	Stage II Vapor Control	5.5E-06 (6.6E-07)[d]	[b]
4-06-006-02	Vehicle Refueling: Spillage	Uncontrolled	3.5E-06 (4.0E-07)[d]	D

[a] Emission factors in lb/gal (kg/l) of gasoline loaded.
[b] No emission factor rating has been assigned.
[c] Ocean barges have a compartment depth of 40 feet; barges have compartment depths of 10-12 feet.
[d] Emission factors in lb/gal (kg/l) of gasoline throughput.

Source: U.S. EPA, 1995; U.S. EPA, 1994a.

Source Locations

Because the sources of emissions in gasoline distribution are so widespread, individual locations are not identified.

SECTION 4.12.7 REFERENCES

Federal Register. Marine Tank Vessel Loading and Unloading Operations and NESHAP for Marine Tank Vessel Loading and Unloading Operations, Notice of Proposed Rulemaking. 59 FR 25004. Government Printing Office, Washington, D.C., May 13, 1994a.

Federal Register. NESHAP for Source Categories: Gasoline Distribution (Stage I), Final Rule. 59 FR 64303. Government Printing Office, Washington, D.C. December 14, 1994b.

U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. Volume I: Stationary Point and Area Sources. AP-42, Fifth Edition. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. pp. 5.2-1 to 5.2-17. 1995.

U.S. Environmental Protection Agency. Gasoline Distribution Industry (Stage I) - Background Information Document for Proposed Standards. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-453/R-94-002a. January 1994a.

U.S. Environmental Protection Agency. Gasoline Distribution Industry (Stage I) - Background Information Document for Promulgated Standards. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-453/R-94-002b. November 1994b.

4.12.8 Rayon-based Carbon Fiber Manufacture

Process Description

Rayon-based carbon fibers are used primarily in cloth for aerospace applications, including phenolic impregnated heat shields and in carbon-carbon composites for missile parts and aircraft brakes (Volk, 1980). Due to their high carbon content, these fibers remain stable at very high temperatures.

There are three steps in the production process of rayon-based carbon cloth (Volk, 1980):

- Preparation and heat treating;
- Carbonization; and
- High heat treatment (optional).

In the preparation and heat treating step, the rayon-based cloth is heated to 390 to 660°F (200 to 360°C). Water is driven off (50 to 60 percent weight loss) during this step to form a char with thermal stability. In the carbonization step, the cloth is heated to 1,830 to 3,630°F (1,000 to 2,000°C), where additional weight is lost and the beginnings of a carbon layer structure is formed. To produce a high strength rayon-based fiber, a third step is needed. The cloth is stretched and heat treated at temperatures near 5,430°F (3,000°C) (Volk, 1980).

Emission Factors

PAH emission factors for rayon-based carbon fiber manufacturing are presented in Table 4.12.8-1. The emission factors are based on a single tested facility. POM emissions were sampled at the exhaust stack of a carbon fabric dryer, which is used in carbonization of heat treated rayon. Both particulate and vapor phase PAHs were quantified (Engineering-Science, Inc., 1990).

TABLE 4.12.8-1. PAH EMISSION FACTORS FOR RAYON-BASED CARBON FIBER MANUFACTURING

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (kg/Mg)[a]	Emission Factor Rating
3-30-001-98	Carbon Furnace	None	Acenaphthylene	1.65E-08 (8.25E-09)	D
			Anthracene	1.25E-08 (6.25E-09)	D
			Fluoranthene	2.48E-08 (1.24E-08)	D
			Fluorene	6.69E-08 (3.34E-08)	D
			Naphthalene	1.74E-05 (8.70E-06)	D
			Phenanthrene	8.12E-08 (4.06E-08)	D
			Pyrene	2.61E-08 (1.30E-08)	D

[a] Emission factors are in lb (kg) per ton (Mg) of carbonized rayon fabric produced.

Source: Engineering-Science, Inc., 1990.

Source Locations

A list of U.S. producers of rayon-based carbon fibers is provided in Table 4.12.8-2.

TABLE 4.12.8-2. RAYON-BASED CARBON FIBER MANUFACTURERS

Manufacturer	Location
Amoco Performance Products, Inc.	Greenville, SC
BP Chemicals (Hitco) Inc. Fibers and Materials Division	Gardena, CA
Polycarbon, Inc.	Valencia, CA

Source: SRI, 1994.

SECTION 4.12.8 REFERENCES

Engineering-Science, Inc. AB2588 Air Pollution Source Testing at Hitco Corporation, Gardena, California. Pasadena, California. 1990.

SRI International. 1994 SRI Directory of Chemical Producers - United States of America. Menlo Park, California. p. 509. 1994.

Volk, H.F. "Carbon Fibers and Fabrics." In: Kirk-Othmer Encyclopedia of Chemical Technology, Volume 4. John Wiley and Sons, New York. p. 622. 1980.

4.12.9 Commercial Charbroilers

Process Description

Commercial scale charbroiling is commonly practiced in the food preparation and service industries. Meat products are charbroiled over a wood charcoal or natural gas (most common) flame to cook them and enhance flavor. Commercial charbroilers are generally uncontrolled or controlled by simple grease extractors.

Emission Factors

PAH emission factors for commercial scale charbroiling are presented in Table 4.12.9-1. A single unit was tested, while broiling hamburger with a fat content ranging from 10 to 21 percent over a natural gas flame. The broiler was equipped with an exhaust hood and baffle-type grease extractor. Sampling for POM was conducted at the exhaust stack of the grease extractor (Rogge et al., 1991).

Source Locations

The locations of commercial scale charbroilers are highly diffuse, and generally correlated to population distribution.

TABLE 4.12.9-1. PAH EMISSION FACTORS FOR COMMERCIAL CHARBROILERS

SCC Number	Emission Source	Control Device	Pollutant	Average Emission Factor in lb/ton (mg/kg)[a]	Emission Factor Range in lb/ton (mg/kg)[a]	Emission Factor Rating
23-02-002-000	Exhaust Stack	None	Benz(a)anthracene	5.90E-04 (2.95E-01)	5.80E-04 - 6.00E-04 (2.90E-01 - 3.00E-01)	D
			Benzo(a)pyrene	3.80E-04 (1.90E-01)	---	D
			Benzo(ghi)perylene	4.80E-04 (2.40E-01)	---	D
			Benzo(k)fluoranthene	3.30E-04 (1.65E-01)	1.20E-04 - 5.40E-04 (6.00E-01 - 2.70E-01)	D
			Fluoranthene	4.70E-04 (2.35E-01)	2.40E-04 - 7.00E-04 (1.20E-01 - 3.50E-01)	D
			Pyrene	9.30E-04 (4.65E-01)	3.80E-04 - 1.40E-03 (1.90E-01 - 7.40E-01)	D

[a] Emission factors are in lb (mg) per ton (kg) of hamburger charbroiled.

Source: U.S. EPA, 1994.

SECTION 4.12.9 REFERENCES

Rogge, W. F., L. M. Holdemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simonelt. "Sources of Fine Organic Aerosol. 1. Charbroilers and Meat Cooking Operations." Environmental Science Technology, 26:6, 1991.

U.S. Environmental Protection Agency. Factor Information Retrieval (FIRE) System Database, Version 2.62. March 1994.

SECTION 5.0
EMISSIONS FROM PRODUCTION AND USE OF NAPHTHALENE

Sources of atmospheric emissions of naphthalene related to its production and use are described in this section. Although naphthalene is a POM, it is different from the other POM species in that, similar to benzene, naphthalene is produced commercially and used as a raw material. In contrast, the other POM species are generated as undesired byproducts; they are not produced intentionally for any commercial use. Moreover, naphthalene is a hazardous air pollutants (HAP) listed separately from POM in Section 112(b) of the Act. As discussed throughout Section 4.0, naphthalene can be formed along with the other POM species and emitted from sources other than those associated with naphthalene production and use. Where naphthalene is generated in notable quantities, emission factors were listed along with those for other significant POM species for that source category. However, this section is focused on quantifying emissions specifically from the production and use of naphthalene.

Emission factors for the production processes are presented where available, and control technologies are described. In some cases, the emissions have been estimated from mathematical models. Hence, to estimate emissions for specific facilities and sources, it is advisable to examine the exact nature of the process used, production volume, and control techniques in place before applying any of the emission factors presented here.

5.1 EMISSIONS FROM NAPHTHALENE PRODUCTION

Naphthalene is produced from either coal tar (a byproduct of coal coking) or petroleum. Approximately 90 percent of the total annual capacity of chemical-grade naphthalene is based on coal tar as a feedstock; the remainder is derived from petroleum refinery streams. A 1985 emissions inventory indicated that 12 coke byproduct recovery plants in the United States have the capacity to produce crude naphthalene (EPA, 1986). Other than these coke byproduct recovery plants, three U.S. companies currently produce chemical-grade naphthalene from either coal tar or petroleum at facilities operating with a total annual capacity of 136,000 tons (123,000 Mg), based on various 1993 estimates (Chemical Marketing Reporter, 1993;

Mannsville Chemical Products Corporation, 1993; SRI International, 1993). A few other companies have produced chemical naphthalene in the past; however, their facilities are closed due to market conditions.

Since the early 1970s, naphthalene capacity and production as a whole has decreased at an average rate of about five percent per year, from 440,000 tons (400,000 Mg) in 1970 to 136,000 tons (123,000 Mg) in 1993 (Mannsville Chemical Products Corporation, 1993). The decline in naphthalene capacity and production is primarily due to competition with ortho-xylene as the feedstock for phthalic anhydride production, which is the major end use of naphthalene. Because ortho-xylene is currently the preferred raw material for phthalic anhydride manufacture, only about 15 percent of phthalic anhydride capacity in the United States is based on naphthalene feed.

5.1.1 Naphthalene from Coal Tar

Process Description--Coke Byproduct Recovery Plants

As described in Section 4.7, naphthalene and other POM emitted throughout byproduct coke plants are undesirable, but the recovery of naphthalene in the byproduct recovery portion of such plants is intentional. This section describes in greater detail the portions of the plant specifically associated with naphthalene production. A detailed flow diagram of a typical coke byproduct recovery plant is shown in Figure 5-1 (U.S. EPA, 1984).

Naphthalene is removed from the coke oven gas stream after it leaves the ammonia absorber. The naphthalene-containing gas is cooled in the final cooler, a tower scrubber in which most of the naphthalene and any entrained tar and vapors are condensed by direct contact with water, thus separating naphthalene from the gas stream before the gas is processed further. The condensed naphthalene floats to the top of the water in the final cooler, is skimmed and collected in open sumps as an impure, yellow-brown slurry containing about 50 to 60 percent water. Separation may be enhanced with a froth flotation separator or similar

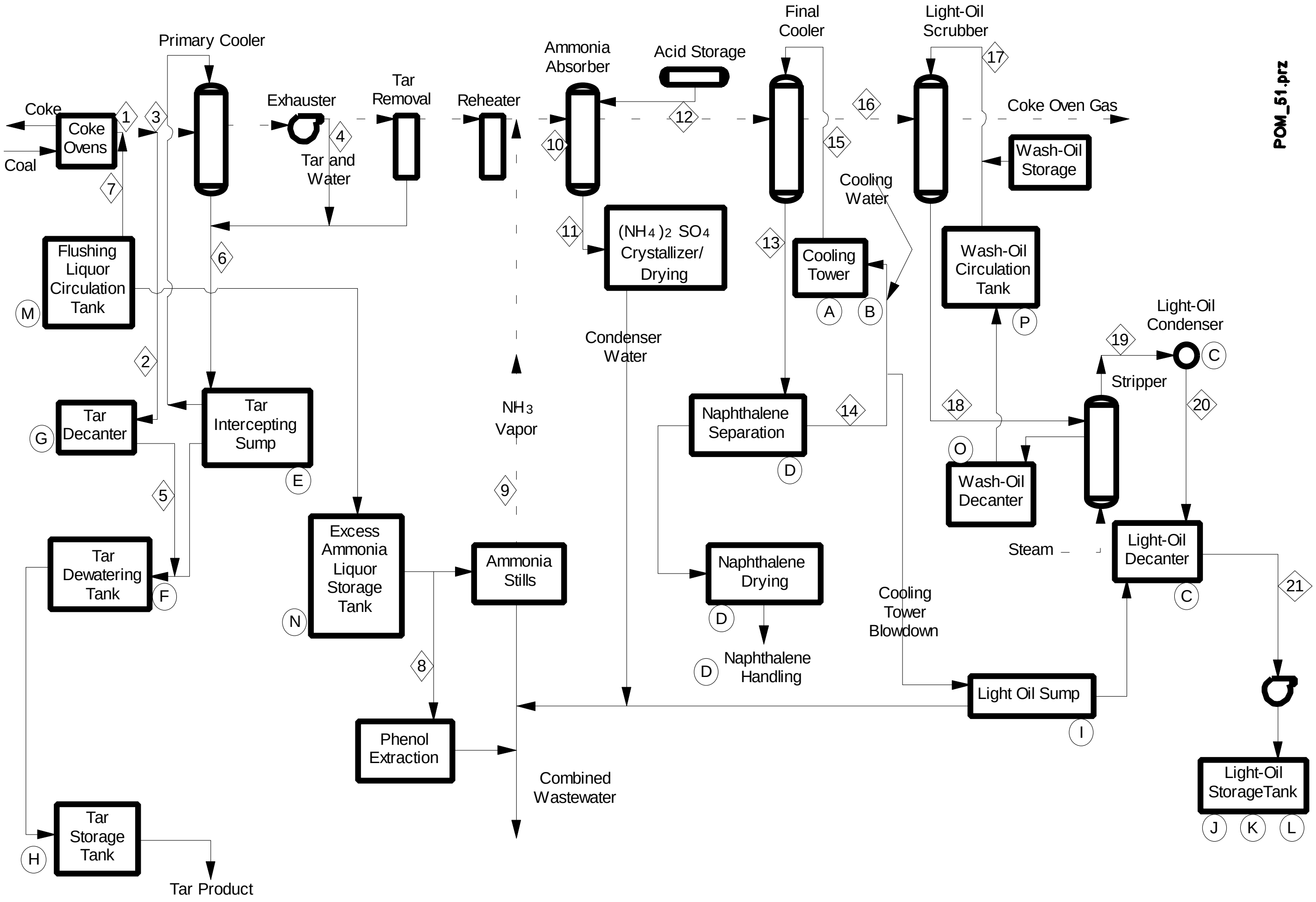


Figure 5-1. Coke Oven Byproduct Recovery, Representative Plant

Source: U.S. EPA, 1984; U.S. EPA, 1979.

equipment. The naphthalene slurry may be pumped into a tank where water is removed by gravity separation, which crystallizes the product.

The resulting crude naphthalene may be dissolved in coal tar after physical separation and sold as a commercial feedstock for making chemical-grade naphthalene. A typical dry coal tar processed in the United States contains approximately 8 to 10 weight percent naphthalene. Although crude naphthalene has little market value, about 40 percent of all coke byproduct recovery plants handle and/or process naphthalene in some manner. If the crude naphthalene is further refined on-site, the crystallized product may be refined through drying when the crystals are melted in a separate rectangular tank equipped with coils for either cold water or steam circulation. After 24 hours in the vessel, a chemical-grade naphthalene is generated.

Emission Factors--Coke Byproduct Recovery Plants

An assessment of naphthalene emissions from all potential sources was made in 1986 to ascertain whether naphthalene should be listed as a Federal HAP (U.S. EPA, 1986). As a part of that assessment, naphthalene emissions from coke byproduct recovery plants were estimated.

Naphthalene emissions can be expected to originate primarily from naphthalene separation and handling in open sumps and naphthalene melting/drying tanks, however, their quantification is difficult. Hence, a naphthalene emission factor for the overall coke byproduct recovery plant was developed, which is based on known annual coke production, the amount of coal tar produced from coke production, and the average naphthalene content of coal tar. This yielded the naphthalene emission factor of 0.012 lb/ton (0.006 kg/Mg) coke produced, which is presented in Table 5-1. According to this emission factor, approximately 80 Mg/yr of naphthalene were emitted in 1986 from coke byproduct recovery plants that process crude naphthalene (53 FR 9139).

TABLE 5-1. NAPHTHALENE EMISSION FACTORS FOR NAPHTHALENE PRODUCTION

SCC Number	Emission Source	Control Device	Naphthalene Emission Factor lb/ton (kg/Mg)	Emission Factor Rating[c]
3-03-003-15	Coke Byproduct Recovery Plant	Uncontrolled	0.012 (0.006)[a]	U
3-03-003-15	Coke Byproduct Recovery Plant	Controlled	0.0024 (0.0012)[a]	U
3-03-003-53	Coal Tar Distillation - Process Emissions	Uncontrolled	0.478 (0.239)[b]	U
3-03-003-36	Coal Tar Distillation - Storage Emissions	Uncontrolled	0.0454 (0.0227)[b]	U

[a] Emission factors in lb/ton (kg/Mg) of coke produced.

[b] Emission factors in lb/ton (kg/Mg) of naphthalene produced.

[c] Factors were assigned a U rating because the supporting documentation for the factors was not sufficient to establish an AP-42 rating using AP-42 factor rating criteria.

Source: EPA, 1986.

In 1986, coke byproduct recovery plants could be expected to be poorly controlled or perhaps uncontrolled. However today, coke byproduct recovery plants are subject to a NESHAP limiting benzene emissions. The controls required by this NESHAP, some of which are described in Section 4.7.3, are estimated to control 80 percent or more of naphthalene emissions. For instance, the standard stipulates that no (“zero”) benzene emissions are allowed from naphthalene processing, final coolers and final-cooler cooling towers (40 CFR 61, Subpart L). In achieving this zero standard, naphthalene emissions are eliminated from these points as well. Hence, the factor reported above may be reduced by 80 percent to 0.0024 lb/ton (0.0012 kg/Mg) coke produced, which may be used as an emission factor for controlled naphthalene emissions from coke byproduct plants.

Source Locations--Coke Byproduct Recovery Plants

As stated previously, not all coke byproduct recovery plants produce crude naphthalene. The majority sell the coal tar containing naphthalene to other companies for further processing. The 12 U.S. coke byproduct recovery plants that were known to handle and/or process so-called coal tar naphthalene in 1985 are listed in Table 5-2 (U.S. EPA, 1986).

Process Description--Coal Tar Distillation

Companies that purchase coal tar do so to recover a number of different products from the coal tar, including chemical-grade naphthalene. The general process for recovering chemical naphthalene from coal tar is by distillation and fractionation (U.S. EPA, 1986). The coal tar is generally distilled in pipe stills in either a batch or continuous process. The tar is charged into a flash tank from which the vapors pass to condensers; the still bottoms and the pitch are sent to receiving tanks. If the total distillate is condensed, the distillate is fractionated into four fractions: light oil (which is a primary source of benzene, toluene, and xylenes), middle oil, heavy oil, and anthracene oil.

TABLE 5-2. U.S. COKE BYPRODUCT RECOVERY PLANTS HANDLING/PROCESSING NAPHTHALENE

Plant	Location
Empire Coke	Holt, AL
Republic Steel	Gadsden, AL
National Steel	Granite City, IL
Interlake	S. Chicago, IL
Indiana Gas and Chemical	Terre Haute, IN
U.S. Steel	Gary, IN
Rouge Steel Co.	Dearborne, MI
National Steel	Detroit, MI
Bethlehem Steel	Bethlehem, PA
Chattanooga Coke and Chemical	Chattanooga, TN
Lone Stare Steel	Lone Star, TX
J&L Steel (LTV Steel)	Pittsburgh, PA

Source: U.S. EPA, 1986.

The middle oil fraction, containing naphthalene, phenols, and cresols, is pumped hot into shallow pans where it is cooled, allowing the naphthalene to crystallize. After draining, the crystalline product is then broken up and charged into batch centrifuges. The mother liquors are combined and sent to phenol and cresol recovery units. The naphthalene product is washed with hot water to increase its purity before it is discharged as crude naphthalene. This material is suitable for phthalic anhydride manufacture and is graded and sold according to its melting point.

For refined naphthalene, the crude material is further distilled. The distillate is first washed with a hot caustic soda solution to remove phenolic compounds and then washed with concentrated sulfuric acid to remove basic substances. To yield a refined product, the washed naphthalene is redistilled. The distillate from the final still is either cast into forms or is cooled and subsequently crushed. The refined material is suitable for manufacture of flakes or pellets for insecticide use (i.e., mothballs or flakes). However, the production of refined naphthalene from coal tar has essentially ceased in the United States due to costs of refining and costs of disposing significant amounts of waste sludge that is generated by the process.

Emission Factors--Coal Tar Distillation

In the 1986 assessment of naphthalene emissions, emission factors for process and storage emissions were developed from emissions inventory data available from one of the facilities that distills naphthalene from coal tar (U.S. EPA, 1986). The facility reported its total POM emissions and total naphthalene production. The total POM emissions were multiplied by a reported estimate of the percent naphthalene content of POM emitted during typical naphthalene production. This estimate of total naphthalene emissions divided by the total naphthalene production reported by the facility yielded a naphthalene emission factor of 0.478 lb/ton (0.239 kg/Mg) naphthalene produced for process emissions from coal tar plants, which is presented in Table 5-1.

An emission factor for naphthalene storage at coal tar plants was similarly calculated from emissions inventory data provided by the facility. The total storage emissions were reported, and a naphthalene storage emission factor was calculated based on the production data from the facility. As listed in Table 5-1, the 1986 assessment presented an emission factor of 0.0454 lb/ton (0.0227 kg/Mg) naphthalene produced for storage emissions from coal tar plants.

The 1986 assessment did not indicate the level of control associated with the facility's reported process and storage emissions. Naphthalene storage vessels can be subject to various NSPS if they meet the specified conditions. On the other hand, naphthalene storage may escape control based on its low vapor pressure (40 CFR 60, Subpart Kb). The recently promulgated Hazardous Organic NESHAP may require control of the process emissions from coal tar distillation. Hence, more precise controlled naphthalene emission factors for coal tar plants may be available in the future after these standards take effect.

Source Locations--Coal Tar Distillation

Facilities other than coke byproduct recovery plants that distill naphthalene from coal tar account for about 90 percent of the total annual chemical-grade naphthalene capacity. There are only two U.S. producers of chemical naphthalene in operation that use coal tar as a raw material: Allied-Signal Inc. in Ironton, Ohio (estimated capacity: 37,500 to 59,500 tons [34,100 to 54,100 Mg]); and Koppers Industries, Inc., in Follansbee, West Virginia (estimated capacity: 75,000 to 85,000 tons [68,200 to 77,300 Mg]).

5.1.2 Naphthalene from Petroleum

Process Description

The production of naphthalene from petroleum, sometimes called petro-naphthalene, involves two principal steps. The first step is the dealkylation, either thermally or catalytically, of a naphthalene/alkyl naphthalene-rich aromatic stream. Second, the naphthalene produced from the dealkylation is recovered as a high-quality product, usually by fractional distillation. Typical feedstocks may be the bottoms fraction of refinery catalytic reformates or a narrow cut distilled and concentrated from refractory cycle oils. Another suitable feedstock may be the stream of naphthalene and methyl naphthalene formed in the cracking of heavy liquids for ethylene production.

The feedstock and a hydrogen-rich gas are pumped to a dealkylation reactor. The reactor product is quenched and is then sent to a separator from which part of the hydrogen-rich gas is recycled and part burned as fuel. The liquid product is distilled to separate fuel gas, gasoline, and naphthalene. The naphthalene produced by this process is usually greater than 99 percent pure and is low in sulfur content.

Emission Factors

In the 1986 assessment of naphthalene emissions from all sources, no data was identified to develop specific emission factors for the production of petro-naphthalene. In the absence of available data, it was assumed in that assessment that the distillation and storage processes for manufacturing petro-naphthalene were similar to those used in coal tar distillation. Hence, the process and storage emission factors for naphthalene production from coal tar that were presented in the previous section were used to estimate annual emissions from petro-naphthalene producers as well.

Source Locations

In 1993, there was only one U.S. producer of chemical naphthalene in operation using petroleum as a raw material: Advanced Aromatics, Baytown, Texas, with a capacity of 10,000 tons (9,100 Mg) (Chemical Marketing Reporter, 1993). A number of companies that produced naphthalene from petroleum in the past are not currently operating, but are capable of restarting if market conditions warrant.

5.2 EMISSIONS FROM END-USES OF NAPHTHALENE

Naphthalene is used almost exclusively as an intermediate in the manufacture of organic chemicals. The only direct use naphthalene is as a moth repellant. Total U.S.

naphthalene consumption is approximately 120,000 to 125,000 tons (110,000 to 114,000 Mg) (Mannsville Chemical Products Corporation, 1993). A 1992 estimate of U.S. naphthalene consumption by end use is as follows (Mannsville Chemical Products Corporation, 1993):

- Phthalic anhydride (64 percent);
- Naphthalene sulfonates (16 percent);
- Carbamate insecticides (10 percent);
- Moth repellent (7 percent); and
- Miscellaneous (3 percent).

Demand for naphthalene and consumption patterns are not expected to change significantly.

A brief description of processes in each of the five major end-uses and the emissions estimated in the 1986 assessment is presented. The reference can be consulted for more detailed descriptions of the different end-uses and the exact description of how emissions for each end-use were calculated.

5.2.1 Phthalic Anhydride Production

Process Description

The overwhelming majority of naphthalene produced is consumed in the manufacture of phthalic anhydride. Phthalic anhydride is derived from one of two raw materials, naphthalene or ortho-xylene. For many years, coal tar naphthalene was the only raw material used for phthalic anhydride production. However, ortho-xylene has gradually replaced naphthalene as the principal feedstock for phthalic anhydride manufacture; today, only about 15 percent of phthalic anhydride is derived from naphthalene (Mannsville Chemical Products Corporation, 1993).

Phthalic anhydride production entails two steps: oxidation and refining. In the oxidation process, coal tar naphthalene and/or o-xylene is vaporized, mixed with air, and fed to the reactors where it is catalytically converted to phthalic acid and other byproducts. It is expected that 100 percent of the feedstock is converted to product so that there are no processing emissions, only storage and fugitive emissions when naphthalene is transferred. Reactor offgases are cooled and sent to a bank of six switch condensers, which capture and solidify the product. According to a preset cycle, one of the condensers is taken out of line and heated to melt out the crude acid which is then transferred to storage. Condenser offgases may be scrubbed using venturi and packed-bed scrubbers before release to the atmosphere.

Phthalic anhydride refining consists of crude storage, decomposing, predistillation, stripping, refining, and refined storage. No naphthalene emissions are expected from the refining step, because all naphthalene is converted. Phthalic anhydride (99.8 percent pure) is then sold or used in polyester production, as a plasticizer, for alkyd resins, and other miscellaneous uses and exports.

Emission Factors

Little or no information is available on naphthalene emission sources from the production of phthalic anhydride. However, all of the end-use industries and the processes involving the use of naphthalene can be considered typical of those found in the synthetic organic chemical manufacturing industries (SOCMI). Hence, emissions can be assumed to originate from three sources: production, fugitive points or equipment leaks, and naphthalene storage. Thus, with the lack of specific data, in the 1986 assessment of naphthalene emissions from all sources, emissions from these various end-uses were estimated using general equipment leak emission factors for the SOCMI, storage vessel emission factors from the EPA's AP-42 document, and the estimate that 0.034 percent of total naphthalene consumed during production each year is emitted to the air. It was estimated that the use of naphthalene to produce phthalic anhydride resulted in emissions of 60 tons (55 Mg) of naphthalene in 1986 (U.S. EPA, 1986).

Source Locations

Since the 1986 assessment, Koppers Company, Cicero, Illinois, has been the only operating naphthalene-based phthalic anhydride plant in the United States. The Koppers facility capacity was estimated at 87,500 tons (79,000 Mg) in 1993 (SRI International, 1993).

5.2.2 Naphthalene Sulfonates Production

Process Description

The second largest end-use of naphthalene is the manufacture of naphthalene sulfonates. Naphthalene sulfonates are generally manufactured by addition of sulfuric acid to naphthalene over heat. Naphthalene sulfonates can be further modified chemically to produce a large mixture of compounds and derivatives. Historically, naphthalene sulfonates were used mainly as synthetic tanning agents, which are used for both vegetable- and chrome-tanned leather. The use of naphthalene sulfonates as tanning agents has declined along with the decline in the domestic leather industry, but increasing use as surface active agents (better known as surfactants) has replaced that demand (U.S. EPA, 1986).

Surfactants are used as wetting agents and dispersants in paints, dyes, pigments, coatings, polymerization emulsifiers, and concrete additives, as well as in a variety of pesticides and cleaner formulations. The application of naphthalene sulfonate compounds, primarily 2-naphthalenesulfonic acid, its alkyl derivatives, and their salts, as surfactants is expected to grow although naphthalene derivatives represent a small portion (less than 0.5 percent) of the total production of surface active agents. The use of these products as concrete additives (i.e., plasticizers) has also increased. Naphthalene sulfonates can increase the flow of concrete without decreasing its strength.

Emission Factors

As with phthalic anhydride, little or no information is available on naphthalene emission sources from the production of naphthalene sulfonates. Therefore, naphthalene emissions were estimated in the 1986 assessment using the estimate that 0.034 percent of total naphthalene consumed during production each year is emitted to the air. Thus, it was estimated from naphthalene consumption data that the production of naphthalene sulfonates accounted for 8.1 tons (7.4 Mg) of naphthalene emissions in 1986 (U.S. EPA, 1986).

Source Locations

There are several different naphthalene sulfonate derivatives produced by a number of companies. It is not always possible to distinguish whether all of a naphthalene sulfonate compound produced at a given facility is intended for use as a synthetic tanning agent or surfactant or some other miscellaneous use. Hence, the location of all producers cannot be identified. The major producers of synthetic tanning agents and surfactants from naphthalene on which the 1986 assessment was based included the companies listed in Table 5-3.

5.2.3 Carbamate Insecticide Production

Process Description

The third largest use of naphthalene is as a raw material for the manufacture of carbamate insecticides, of which carbaryl (Arylam® or better known as Sevin®) is the most important. Carbaryl is used as a substitute for DDT and other chlorinated compounds that have become environmentally unacceptable. It is registered for use on about 70 crops and is used chiefly in the southern and western United States.

Crude or semi-refined coal tar or petroleum naphthalene can be used for carbaryl manufacture. Production involves the following steps: (1) hydrogenation of naphthalene to produce 1,2,3,4-tetrahydronaphthalene, (2) oxidation of this compound to produce 1-naphthol,

TABLE 5-3. MAJOR PRODUCERS OF NAPHTHALENE-BASED SYNTHETIC TANNING AGENTS AND SURFACE ACTIVE AGENTS

Naphthalene End-Use	Plant	Location
Synthetic Tanning Agents	Morflex, Inc.	Greensboro, NC
	Diamond Shamrock	Carlstadt, NJ
		Cedartown, GA
	Georgia-Pacific	Bellingham, WA
	Rohm and Haas	Philadelphia, PA
Surface Active Agents	American Cyanamid	Marietta, OH
		Linden, NJ
	Ciba-Geigy	Toms River, NJ
	DeSoto, Inc.	Fort Worth, TX
	Diamond Shamrock	Carlstadt, NJ
		Cedartown, GA
	Emkay Chemicals	Elizabeth, NJ
	Morflex, Inc.	Greensboro, NC
	Georgia-Pacific	Bellingham, WA

Source: U.S. EPA, 1986.

and (3) reaction of 1-naphthol with methyl isocyanate to produce 1-naphthyl-n-methyl carbamate (carbaryl). Intermediate products of this process, 1,2,3,4-tetrahydronaphthalene and 1-naphthol, are also used as insecticides.

Emission Factors

Again, little information is available on naphthalene emission sources from the production of carbamate insecticides. Therefore, naphthalene emissions were estimated in the 1986 assessment using emissions inventory data provided by the sole U.S. carbaryl producer. The data indicate that the production of carbaryl accounted for 5.0 tons (4.6 Mg) of naphthalene emissions in 1986. If specific information for the plant can be obtained, equipment leak emission factors for the SOCMI, storage vessel emission factors from EPA's AP-42 document, or the estimate that 0.034 percent of total naphthalene consumed during production each year is emitted to the air could be used to check this estimate.

Source Locations

Rhone-Poulenc at Institute, West Virginia, is the only domestic producer of carbaryl, having purchased the business from Union Carbide in 1987.

5.2.4 Moth Repellant Production

Process Description

The manufacture of moth repellant accounts for the fourth largest use of naphthalene. The production of naphthalene-based moth repellant has decreased, however, due to the availability of para-dichlorobenzene and the increased use of synthetic fibers. Moth repellant is the only consumer product manufactured directly from naphthalene. The product is manufactured as a solid flake, powder, or ball, and repackaged for shipment. All of the naphthalene contained in moth repellant is emitted to the atmosphere.

Emission Factors

It was assumed in the 1986 assessment that because production of moth repellant only involved repackaging naphthalene in the solid form, no process, fugitive, or storage emissions were expected. Hence, no emissions were estimated for this use of naphthalene. However, if it is discovered that the manufacture does involve processing of naphthalene in the liquid form, equipment leak emission factors for the SOCMI, storage vessel emission factors from EPA's AP-42 document, or the estimate that 0.034 percent of total naphthalene consumed during production each year is emitted to the air could be used to estimate emissions (U.S. EPA, 1986).

Source Locations

Two producers of naphthalene-based moth repellant were identified in the 1986 assessment: Morflex, Inc. of Greensboro, North Carolina, and Kincaid Enterprises of Nitro, West Virginia (U.S. EPA, 1986).

5.2.5 Miscellaneous Uses

Process Description

Approximately 3 percent of naphthalene consumption is used in the manufacture of various organic chemicals and intermediates. There are numerous miscellaneous naphthalene derivatives including the following:

- Alkylnaphthalenes;
- Chlorinated naphthalenes;
- Hydrogenated naphthalenes;
- Naphthalenecarboxylic acids;

- Nitronaphthalenes;
- Naphthylamines;
- Naphthols; and
- Aminonaphthols.

These chemicals are produced in relatively small amounts and cannot be separately quantified.

Emission Factors

As with naphthalene sulfonate compounds, there are several miscellaneous naphthalene derivatives produced by a number of companies. Naphthalene emissions were again estimated in the 1986 assessment from the naphthalene consumption by a few major endusers using the estimated factor of 0.034 percent of total naphthalene consumed during production each year is emitted to the air. It was estimated that the production of naphthalene sulfonates accounted for 1.5 tons (1.4 Mg) of naphthalene emissions in 1986.

Source Locations

In 1986, the major producers of miscellaneous naphthalene chemicals on which the 1986 assessment was based included the companies listed in Table 5-4.

TABLE 5-4. MAJOR PRODUCERS OF MISCELLANEOUS NAPHTHALENE-BASED CHEMICALS

Plant	Location
Chemical Exchange	Houston, TX
Ciba-Geigy	Toms River, NJ
Koppers Company	Follansbee, WV
RSA Corporation	Ardsley, NY
Sigma Chemical Company	St. Louis, MO
Union Carbide	Ambler, PA
Uniroyal, Inc.	Gastonia, NC

Source: U.S. EPA, 1986.

SECTION 5.0 REFERENCES

Chemical Marketing Reporter. Naphthalene. December 13, 1993.

Code of Federal Regulations. 40 CFR Part 60, Subpart Kb, "Standards of Performance for Volatile Organic Liquid Storage Vessels (including Petroleum Liquid Storage Vessels) for which Construction, Reconstruction, or Modification Commenced after July 23, 1984."

Code of Federal Regulations. 40 CFR Part 61, Subpart L, "National Emission Standard for Benzene Emissions from Coke Byproduct Recovery Plants."

Federal Register. Assessment of Naphthalene As a Potentially Toxic Air Pollutant. 53 FR 9139. Government Printing Office, Washington, D.C. March 21, 1988.

Mannsville Chemical Products Corporation. Naphthalene. "Chemical Products Synopsis." Asbury Park, New Jersey. March 1993.

SRI International. 1993 Directory of Chemical Producers. Menlo Park, California. 1993.

U.S. Environmental Protection Agency. Summary of Emissions Associated with Sources of Naphthalene. Emission Standards Division, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/3-88-003. October 30, 1986.

U.S. Environmental Protection Agency. Benzene Emissions from Coke Byproduct Recovery Plants - Background Information Document for Proposed Standards. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/3-83-016a. May 1984.

U.S. Environmental Protection Agency. Environmental Assessment of Coke Byproduct Recovery Plants. Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. EPA-600/2-79-016. January 1979.

SECTION 6.0

SOURCE TEST PROCEDURES

Several sampling and analytical techniques have been employed for the quantification of POM. The selection of sampling and analytical techniques is driven by the nature of the emissions source, the quantity of POM present, and the specific POM compounds of interest. The following methods are applicable for measuring POM emissions from stationary sources, ambient air, and vehicle exhaust:

- EPA Method 0010: Modified Method 5 Sampling Train;
- EPA Method 8270: Gas Chromatography/Mass Spectrometry (GC/MS) for Semivolatile Organics, Capillary Column Technique;
- EPA Method 8310: Polynuclear Aromatic Hydrocarbons by High Performance Liquid Chromatography (HPLC);
- EPA Method TO-13: Determination of Polynuclear Aromatic Hydrocarbons (PAHs) in Ambient Air Using High Volume Sampling with GC/MS and HPLC; and
- EPA Exhaust Gas Sampling System, Federal Test Procedure (FTP).

6.1 EPA METHOD 0010

EPA Method 0010 (Modified Method 5 Sampling Train [MM5]) is used to determine the destruction and removal efficiency of semi-volatile principal organic hazardous constituents (POHCs) from incineration systems and other stationary sources. This method may be used for determining POM emissions.

The MM5 sampling train is an adaptation of the EPA Method 5 train used in measuring particulate emissions (U.S. EPA, 1986; U.S. EPA, 1991). The modifications are the addition of a condenser and a sorbent module between the filter and the impingers. The condenser cools the gas stream leaving the filter and conditions the streams prior to entering the sorbent module.

Gaseous and particulate pollutants are withdrawn isokinetically from an emissions source and collected in a multicomponent sampling train. Figure 6.1-1 presents a schematic of the sampling system. Principal components of the train include a high-efficiency glass- or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin (typically XAD-2® for POM emissions). The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semivolatile organic species (compounds with a boiling point above 100°C). It should be noted that the XAD-2® must be carefully cleaned to avoid contamination from naphthalene, a XAD-2® artifact. In addition, the sorbent module should be wrapped in aluminum foil to protect it from light, which can adversely affect analysis.

The MM5 train is designed to operate at flow rates of approximately 0.015 dry standard cubic meter per minute (dscmm) (0.5 dscfm) over a 4-hour sampling period. Sample volumes of 3 dscm (100 dscf) are typical, although the volume that is sampled will vary according to the analyte. Because method detection limits are a function of volume sampled, this will also vary.

The entire sorbent module with filter is typically extracted with methylene chloride. The extract must not contain any moisture or methanol, or the analyses will be compromised. The extract is concentrated to 5 milliliters (mL) (a final volume of 5 mL is used to avoid loss of volatile compounds) and this final extract volume represents the entire volume of gas sampled. It should also be noted that when extracting the rinse solutions from the impingers, sufficient water must be added to separate the methanol from the methylene chloride.

After sampling and extraction, comprehensive chemical analyses using a variety of applicable analytical methodologies are conducted to determine the identity and concentration of the organic materials.

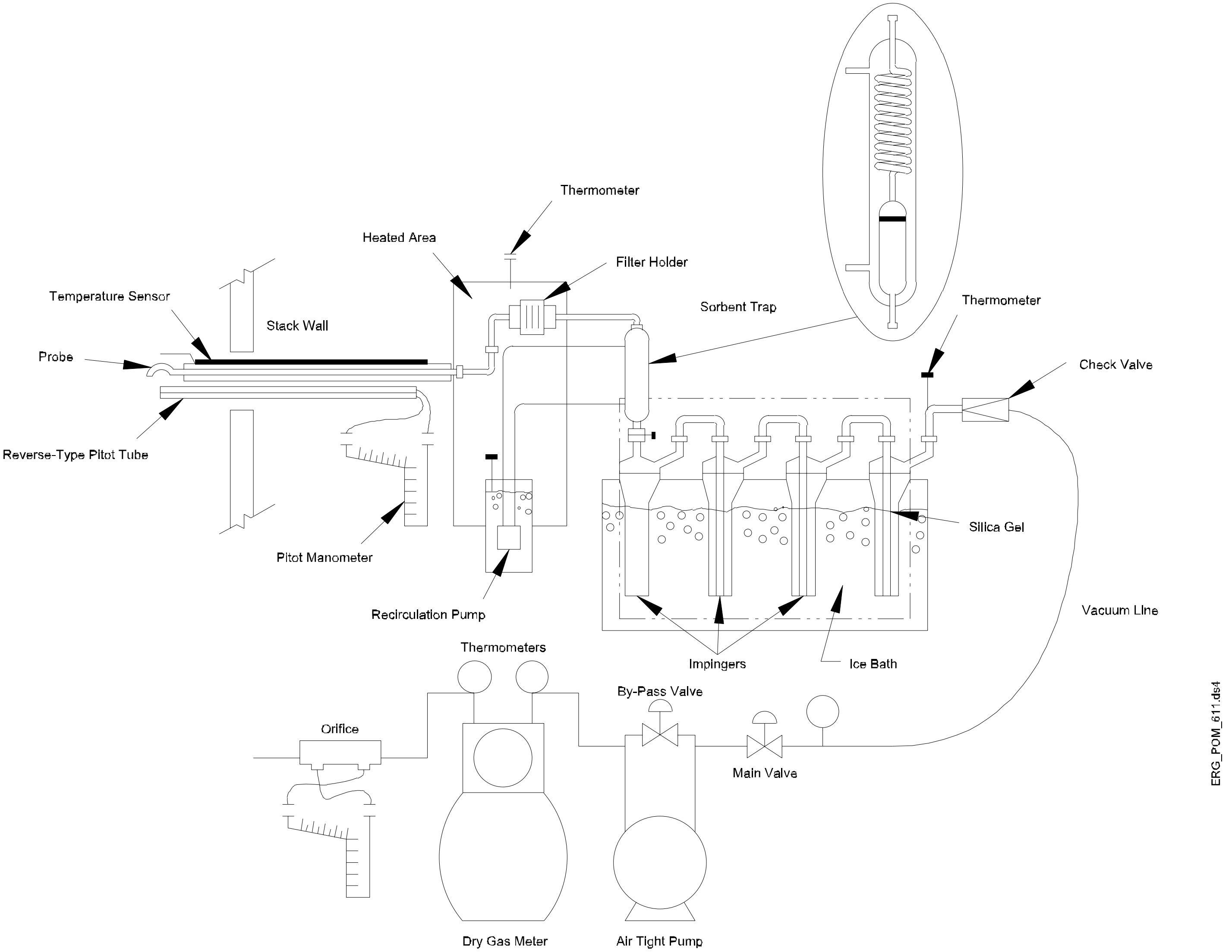


Figure 6.1-1. Modified Method 5 Sampling Train (EPA Method 0010)

Source: U.S. EPA, 1986.

A major advantage of the MM5 train is that the method provides both a quantitative sample for POM analysis and a determination of particulate loading (front-half filterable particulates) comparable to EPA Method 5. A disadvantage is that long sampling periods are required to collect enough sample to support chemical analysis.

When GC/MS is used as the analytical technique, compounds that coelute chromatographically can frequently be deconvoluted if their mass spectra are different. Using two or more ions per compound in quantitative analysis can overcome interference at one mass; however, if the concentration of the compound of interest is sufficient to saturate the detector at a given mass, an alternative mass may not be selected. In this case, the extract must be diluted to bring the concentration of the compound of interest into the calibration range in order to obtain accurate quantitative analysis (U.S. EPA, 1991).

6.2 EPA METHOD 8270

EPA Method 8270 is a GC/MS method used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and groundwater (U.S. EPA, 1986; U.S. EPA, 1991). It is also applicable to an extract (such as POM) from sorbent media in conjunction with Method 0010. The practical quantitation limit for Method 8270 is approximately 50 µg/mL of extract. Direct injection of a sample may be used in limited applications.

Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. POM compounds are within the boiling point range and may be determined using this methodology.

EPA Method 8270 describes conditions for capillary column GC/MS to allow for the separation of semivolatile compounds. Sample extraction, purification, and concentration techniques are addressed in other methods. For example, EPA Methods 3510, 3520, 3540, 3550, and 3580 may be applicable to POM sample preparation. (U.S. EPA, 1991) The following purification methods may be used prior to GC/MS analysis: EPA Methods 3611, 3630, and 3640 (U.S. EPA, 1991).

Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference results from the preparation and/or cleanup of samples, corrective action can be taken to eliminate the problem. If the problem is a very high sample background of alkyl or aromatic hydrocarbons, very little can be done to resolve the problem other than dilution of the samples, which raises the detection limit. If chromatographic coelution occurs, deconvolution of the coeluting components by mass spectrometric techniques will be effective if the compounds are not chemically related and their mass spectra can be resolved. If isomers coelute and their mass spectra are similar, the coelution cannot be resolved (U.S. EPA, 1991).

Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. To reduce carryover, the sample syringe must be rinsed carefully with solvent between sample injections. The chromatographic column should be allowed to remain at a high temperature until all late-eluting components have eluted from the column in order to avoid chromatographic carryover problems. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of clean solvent to check for cross-contamination. If contamination is observed, the injections of solvent should be repeated until the contamination is no longer observed before another sample injection is performed (U.S. EPA, 1991).

6.3 EPA METHOD 8310

EPA Method 8310 is used to determine the concentration of certain PAHs in groundwater and wastes at parts-per-billion levels (U.S. EPA, 1986; U.S. EPA, 1991). By extension, the methodology should be applicable to material extracted from a solid sorbent module of a sampling train from EPA Method 0010, which is used to sample gaseous emissions from a stationary source.

Extension of the methodology to PAHs containing functional groups should be possible, depending upon the ability to adjust analytical conditions and the availability of standards for the compounds of interest.

Prior to using Method 8310, appropriate sample extraction methods must be used. A 5- to 25-µL aliquot of extract is injected into an HPLC, and compounds in the effluent are detected by ultraviolet (UV) and fluorescence detectors. If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone purification using silica gel column cleanup (EPA Method 3630).

Use of Method 8310 presupposes a high expectation of finding the specific compounds of interest. To screen samples for any or all of the method target compounds, independent protocols for the verification of identity must be developed. One method that can be used to certify identity is GC/MS.

Method detection limits are compound-dependent, ranging from 0.4 µg/L for indeno(1,2,3-cd)pyrene in groundwater to 230,000 µg/L for acenaphthylene in non-water miscible waste. Detection limits for PAHs in gaseous emissions have not been determined directly. This methodology has not been directly and specifically applied to the determination of POM other than the PAHs specifically listed in the methodology. A quantitative analysis of other PAHs and functionalized PAHs will require adjustment of analytical conditions and the use of appropriate standards. An additional method such as GC/MS, if applicable, may be required to identify additional compounds (U.S. EPA, 1991).

If coelution of compounds is encountered in samples taken from gaseous emissions of stationary sources, Method 8310 may not be applicable unless analytical conditions can be adjusted to achieve chromatographic resolution.

The sensitivity of the method usually depends on the level of interferences rather than instrumental limitations. The limits of detection mentioned earlier for the liquid chromatographic approach represent sensitivities that can be achieved in the absence of interferences. When interferences are present, the level of sensitivity will be lower, if analysis is possible at all (U.S. EPA, 1991).

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

Interferences coextracted from the samples will vary considerably from source to source. Although a general cleanup technique is provided as part of Method 8310, individual samples may require additional cleanup approaches to achieve the desired sensitivity.

The chromatography conditions described in Method 8310 allow for a unique resolution of the specific PAH compounds covered by this method. Other PAH compounds, in addition to matrix artifacts, may interfere.

6.4 EPA METHOD TO-13

Method TO-13 describes sampling and analytical techniques used to determine benzo(a)pyrene and other PAHs in ambient air. Nitro-PAHs are not included with this method. In Method TO-13, air is drawn through a filter and adsorbent cartridge containing XAD-2® or polyurethane foam (PUF). As with EPA Method 0010, the XAD-2® resin must be carefully cleaned to avoid contamination from naphthalene, and the adsorbents should be protected from light during sampling and storage. In addition, the quality of PUF will vary markedly from lot to lot, so every effort should be made to obtain PUF from the same production lot for sampling at a single site.

The filters and adsorbents are extracted, and the extract is subjected to cleanup with silica gel column chromatography. The sample is further concentrated and analyzed by either gas chromatography equipped with flame ionization detector or a mass spectrometer, or HPLC.

The relatively low level of PAHs in the environment requires use of high-volume (approximately 6.7 cfm) sampling techniques to acquire sufficient sample for analysis. However, the volatility of certain PAHs prevents efficient collection on filter media alone. Consequently, this method utilizes both a filter and a backup adsorbent cartridge, which provide for efficient collection of most PAHs (U.S. EPA, 1988).

Method interferences may be caused by contaminants in solvents, reagents, glassware, and sampling hardware. Matrix interferences may be caused by contaminants that are coextracted with the sample. Heat, ozone, nitrogen dioxide, and UV light may cause sample degradation.

Detection limits for GC and HPLC methods range from 1 ng to 10 pg, which represents detection of PAHs in filtered air at levels below 100 pg/m^3. To obtain this detection limit, at least 100 m^3 of air must be sampled (U.S. EPA, 1988).

6.5 FEDERAL TEST PROCEDURE (FTP)

The most widely-used test procedure for sampling emissions from vehicle exhaust is the FTP, which was initially developed in 1974 (40 CFR 86, Subpart B; Blackley Telecon, 1994a and 1994b). The FTP uses the Urban Dynamometer Driving Schedule (UDDS), which is 1,372 seconds in duration. An automobile is placed on a chassis dynamometer, where it is run according to the following schedule: 505 seconds of cold-start; 867 seconds of hot transient; and 505 seconds of hot-start. (Definitions of the above terms can be found in the FTP description in the 40 CFR, Section 86, Subpart B). The vehicle exhaust is collected in three separate teflon bags associated with backup filters/adsorbents for each of the three testing stages.

The most widely used method for transporting vehicle exhaust from the vehicle to the bags is a dilution tube sampling arrangement identical to the system used for measuring criteria pollutants from mobile sources (40 CFR 86, Subpart B; Smith, 1988). Dilution techniques are used for sampling auto exhaust because, in theory, dilution helps simulate the conditions under which exhaust gases condense and react in the atmosphere. Figure 6.5-1 shows a diagram of a vehicle exhaust sampling system (Lee and Schuetzle, 1985). Vehicle exhausts are introduced at an orifice where the gases are cooled and mixed with a supply of filtered dilution air. The diluted exhaust stream flows at a measured velocity through the dilution tube and is sampled isokinetically.

The major advantage in using a dilution tube approach is that exhaust gases are allowed to react and condense onto particle surfaces prior to sample collection, providing a truer composition of exhaust emissions as they occur in the atmosphere. Another advantage is that the dilution tube configuration allows simultaneous monitoring of hydrocarbons, CO, CO_2, and NO_x. Back-up sampling techniques, such as filtration/adsorption (e.g., XAD-2®, Chromsorb 102, or Tenax®), are generally recommended for collection of both particulate- and gas-phase emissions (Blackley Telecon, 1994b). This is a particularly true for POM, which is often found in particulate form in vehicle exhaust.

After the exhaust samples are collected, extraction using EPA Method 3540 is recommended, followed by analysis using EPA Method 8270, described earlier.

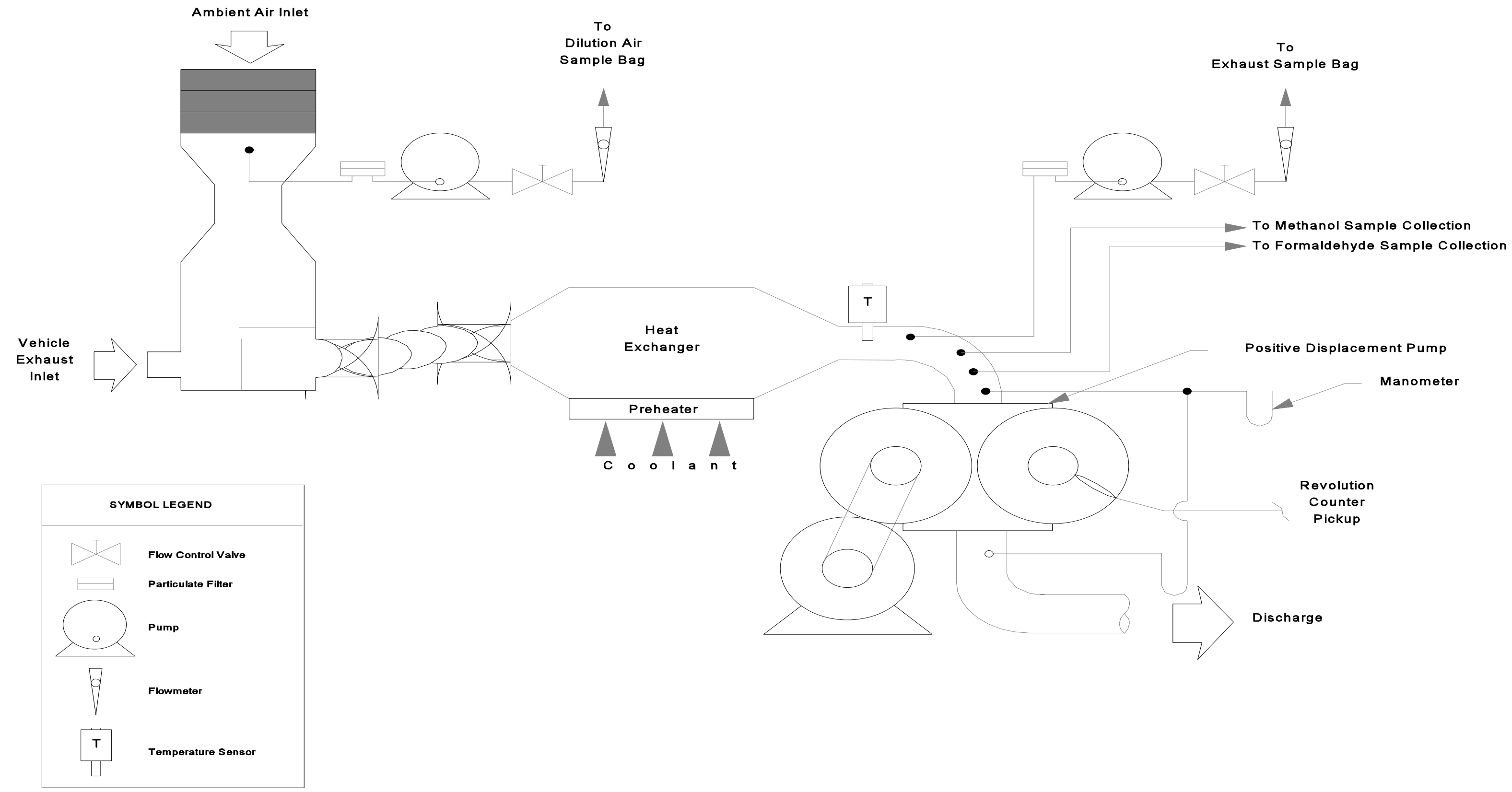


Figure 6.5-1. Vehicle Exhaust Gas Sampling System

Source: Lee, 1985.

SECTION 6.0 REFERENCES

C. Blackley, Radian Corporation, telephone communication with R. Zweidinger, U.S. Environmental Protection Agency. May 10, 1994. 1994a.

C. Blackley, Radian Corporation, telephone communication with P. Gabele, U.S. Environmental Protection Agency. May 10, 1994. 1994b.

Code of Federal Regulations, 40 CFR Part 86, Subpart B. “Emission Regulations for 1977 and Later Model Year New Light-Duty Vehicles and New Light-Duty Trucks; Test Procedures.” December 10, 1993.

Lee, F.S., and D. Schuetzle. “Sampling, Extraction, and Analysis of Polycyclic Aromatic Hydrocarbons from Internal Combustion Engines.” In: Handbook of Polycyclic Aromatic Hydrocarbons, A. Bjorseth, ed. Marcel Dekker, Inc., New York. p. 30. 1985.

Smith, Lawrence R. Butadiene Measurement Technology. EPA-460/3-88-005. August 1988.

U.S. Environmental Protection Agency. Screening Methods for Development of Air Toxics Emission Factors. Research Triangle Park, North Carolina. EPA-450/4-91-021. September 1991.

U.S. Environmental Protection Agency. 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-600/4-89-017. June 1988.

U.S. Environmental Protection Agency. Test Methods for Evaluating Solid Waste. Office of Solid Waste and Emergency Response, Washington, DC. Third Edition, Report No. SW-846. November 1986.

APPENDIX A

SUMMARY OF 7-PAH AND 16-PAH EMISSION FACTORS

Table A-1 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 Table A-1 do not represent all the potential POM source categories discussed earlier in this document. The EPA did not always have activity levels to match to the available emission factors for every source category, so Table A-1 only contains those categories for which an activity level was available to calculate national emissions.

The 16-PAH factors represent the sum of the emission factors for the following individual PAHs, where available, for each source category:

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

The pollutants with asterisks (*) correspond to the subset of seven PAHs for which emission factors were summed, where available, for each source category to obtain the 7-PAH emission factor.

For each source category there was not always a complete set of the seven or sixteen PAH emission factors in order to compile the 7-PAH and 16-PAH factors, respectively. Therefore, the 7-PAH and 16-PAH emissions are not directly comparable across all source categories.

For most of the source categories listed in Table A-1, 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 presented in Table A-1 for these source categories were developed by EPA specifically for the purpose of the national emission inventory effort in support of the Section 112(c)(6) study and were not derived from the emission factor tables contained in this document. 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). The reader is referred to the documentation for the 112(c)(6) inventory effort for details on how the 16-PAH and 7-PAH factors were developed for each source category, including the “Ferroalloy Manufacturing” and “Onroad Vehicles” sources (U.S. EPA, 1998).

When using the emission factors in Table A-1, the user should keep in mind that these were developed to be representative of nationwide activity and do not, in most 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 where available in previous sections of this document.

TABLE A-1. SUMMARY OF EMISSION FACTORS FOR 7-PAH[a] AND 16-PAH[b] SUBSETS BY SOURCE CATEGORY

Source Category	7-PAH Emission Factor[c]	16-PAH Emission Factor[d]
STATIONARY EXTERNAL COMBUSTION		
Residential Heating		
Residential Wood Combustion		
Conventional Woodstoves	0.044 lb/ton wood burned	0.718 lb/ton wood burned
Catalytic/Noncatalytic Stoves	0.048 lb/ton wood burned	0.627 lb/ton wood burned
Fireplaces	0.007 lb/ton wood burned	0.037 lb/ton wood burned
Residential Natural Gas Combustion	0.0373 lb/1E+12 Btu of heat input	2.37 lb/1E+12 Btu of heat input
Residential Distillate Oil Combustion	5.63E-04 lb/1,000 gal of fuel consumed	6.97E-03 lb/1,000 gal of fuel consumed
Residential Coal Combustion (bituminous and lignite)	0.0335 lb/ton of coal consumed	0.108 lb/ton of coal consumed
Residential Coal Combustion (anthracite)	1.41E-04 lb/ton of coal consumed	6.18E-04 lb/ton of coal consumed
Utility, Industrial, and Commercial Boilers		
Industrial Wood/Wood Residue Combustion	5.90E-05 lb/ton of wood burned	3.36E-03 lb/ton of wood burned
Industrial Natural Gas Combustion	ND	5.56E-06 lb/MMCF of natural gas consumed
Industrial Coal Consumption	5.36E-05 lb/ton of coal consumed	2.72E-03 lb/ton of coal consumed
Industrial Residual Oil Combustion	1.60E-07 lb/MMBtu of heat input	2.15E-04 lb/MMBtu of heat input
Industrial Distillate Oil Combustion	5.96E-09 lb/MMBtu of heat input	5.00E-05 lb/MMBtu of heat input
Industrial Waste Oil Combustion	4.53E-03 lb/1,000 gallons of waste oil consumed	0.0265 lb/1,000 gallons of waste oil consumed
Commercial Wood/Wood Residue Combustion	7.43E-05 lb/MMBtu of heat input	2.63E-03 lb/MMBtu of heat input
Commercial Natural Gas Combustion	ND	2.54E-05 lb/MMCF of natural gas consumed
Commercial Coal Combustion (bituminous and lignite)	0.0200 lb/ton of coal consumed	0.0771 lb/ton of coal consumed
Commercial Coal Combustion (anthracite)	ND	0.137 lb/ton of coal consumed
Commercial Residual Oil Combustion	1.60E-07 lb/MMBtu of heat input	2.14E-04 lb/MMBtu of heat input
Commercial Distillate Oil Combustion	5.96E-09 lb/MMBtu of heat input	5.00E-05 lb/MMBtu of heat input
STATIONARY INTERNAL COMBUSTION		
Industrial IC Engines		
Industrial IC Engines - Diesel	3.36E-06 lb/MMBtu of heat input	1.89E-04 lb/MMBtu of heat input
Industrial IC Engines - Natural Gas	2.75E-03 lb/MMCF of natural gas consumed	0.127 lb/MMCF of natural gas consumed

(continued)

TABLE A-1. (Continued)

Source Category	7-PAH Emission Factor[c]	16-PAH Emission Factor[d]
Turbines		
Turbines - Diesel	ND	1.03E-07 lb/MMBtu of heat input
Turbines - Natural Gas	ND	4.90E-05 lb/MMBtu of heat input
WASTE INCINERATION		
Municipal Waste Incineration	ND	6.07E-06 lb/ton of waste incinerated
Sewage Sludge Incineration	1.822E-05 lb/ton of sludge incinerated	3.44E-03 lb/ton of sludge incinerated
Medical Waste Incineration	ND	9.22E-04 lb/ton of waste incinerated
Hazardous Waste Incineration	2.91E-05 lb/ton of hazardous waste incinerated	2.44E-04 lb/ton of hazardous waste incinerated
Drum and Barrel Reclamation	5.53E-07 lb/1,000 barrels reclaimed	3.56E-05 lb/1,000 barrels reclaimed
Scrap Tire Incineration	1.68E-03 lb/1E+06 tires incinerated	0.40 lb/1E+06 tires incinerated
Landfill Flares	3.08E-08 lb/MMBtu of heat input	1.30E-05 lb/MMBtu of heat input
METALS INDUSTRY		
Primary Aluminum Production		
Horizontal Stud Soderberg Cells	0.058 lb/ton aluminum produced	0.59 lb/ton aluminum produced
Vertical Soderberg Cells	0.12 lb/ton aluminum produced	0.49 lb/ton aluminum produced
Vertical Pre-bake Cells	0.0013 lb/ton aluminum produced	0.0073 lb/ton aluminum produced
Casting Operations	3.64E-04 lb/ton aluminum produced	1.30E-02 lb/ton aluminum produced
Paste Production	0.0019 lb/ton aluminum produced	0.015 lb/ton aluminum produced
Anode Bake Furnaces	0.05 lb/ton aluminum produced	0.135 lb/ton aluminum produced
Sintering in the Iron and Steel Foundries	ND	ND
Ferroalloy Manufacturing[e]		
Wood-fired Open EAFs	8.24E-04 lb/ton wood consumed	1.75E-03 lb/ton wood consumed
Coal-fired Open EAFs	2.32E-03 lb/ton coal consumed	5.04E-03 lb/ton coal consumed
Coke-fired Open EAFs	2.32E-04 lb/ton coke consumed	5.03E-04 lb/ton coke consumed
Iron Foundries	2.07E-05 lb/ton of metal produced	6.21E-05 lb/ton of metal produced
Secondary Lead Smelting - Blast Furnaces	ND	0.0199 lb/ton of lead produced
Secondary Lead Smelting - Rotary and Blast/Reverb Furnaces	3.7E-05 lb/ton of lead produced	5.1E-05 lb/ton of lead produced
PETROLEUM REFINING		
Catalytic Cracking	1.66E-05 lb/barrel of oil charged	3.16E-04 lb/barrel of oil charged
ASPHALT PRODUCTION		
Asphalt Roofing Production	1.1E-04 lb/ton of asphalt roofing produced	2.86E-03 lb/ton of asphalt roofing produced
Asphalt Hot-mix Production	3.90E-07 lb/ton of hot-mix asphalt produced	1.82E-04 lb/ton of hot-mix asphalt produced

(continued)

TABLE A-1. (Continued)

Source Category	7-PAH Emission Factor[c]	16-PAH Emission Factor[d]
COKE PRODUCTION		
Coke Ovens: Charging, Topside, and Door Leaks	3.72E-03 lb/ton of coal charged	2.79E-02 lb/ton of coal charged
Coke Ovens: Pushing, Quenching, and Battery Stacks	3.09E-03 lb/ton of coal charged	0.053 lb/ton of coal charged
PORTLAND CEMENT MANUFACTURING		
Non-hazardous Waste Kilns	8.21E-05 lb/ton clinker produced	1.51E-03 lb/ton clinker produced
Hazardous Waste Kilns	2.52E-04 lb/ton clinker produced	1.53E-03 lb/ton clinker produced
PULP AND PAPER INDUSTRY		
Kraft Recovery Furnaces	1.23E-04 lb/air-dry ton of pulp produced	0.0213 lb/air-dry ton of pulp produced
Lime Kilns	3.3E-06 lb/MMBtu of heat input	2.46E-03 lb/MMBtu of heat input
Sulfite Recovery Furnaces	ND	4.30E-03 lb/air-dry ton of pulp produced
OPEN BURNING		
Wildfires and Prescribed Burning	0.020 lb/ton of biomass burned	0.053 lb/ton of biomass burned
Open Burning of Scrap Tires	1,400 lb/1,000 tons of tire burned	7,850 lb/1,000 tons of tire burned
MOBILE SOURCES		
Onroad Vehicles[e]	14.52 μg/vehicle miles of travel	32.08 μg/vehicle miles of travel
Aircraft	1.09E-05 lb/LTO	3.06E-04 lb/LTO
Locomotives	ND	ND
Marine Vessels	ND	ND
Non-road Vehicles and Equipment	ND	ND
MISCELLANEOUS SOURCES		
Carbon Black Manufacturing	5.25E-04 lb/ton of carbon black produced	5.04E-03 lb/ton of carbon black produced
Wood Treatment/Wood Preserving	ND	1.94E-03 lb/ft^3 of wood treated
Cigarette Smoke	2.08E-09 lb/cigarette consumed	1.38E-08 lb/cigarette consumed
Crematories	7.07E-11 lb/body cremated	4.16E-08 lb/body cremated
Gasoline Distribution	ND	NA
Carbon Fiber Manufacturing	NA	NA
NAPHTHALENE PRODUCTION AND USE		
Naphthalene Production	ND	0.523 lb/ton of naphthalene produced 0.0024 lb/ton of coke produced
Phthalic Anhydride Production	ND	0.34 lb/1,000 lb naphthalene consumed
Carbamate Insecticides Production	ND	0.34 lb/1,000 lb naphthalene consumed

(continued)

TABLE A-1. (Continued)

Source Category	7-PAH Emission Factor[c]	16-PAH Emission Factor[d]
Naphthalene Sulfonates Production	ND	0.34 lb/ 1,000 lb naphthalene consumed
Miscellaneous Uses	ND	0.34 lb/1,000 lb naphthalene consumed

[a] 7-PAH subset includes benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene.

[b] 16-PAH subset includes acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene.

[c] All 7-PAH are not included in the 7-PAH factor for every source category; in some cases, there is not a complete set of factors for all 7-PAH since the available test data did not report or sample for a specific PAH compound(s). Refer to the documentation for the Section 116(c)(6) inventory development for a listing of the specific compounds included in the 7-PAH emission factor for a particular source category (U.S. EPA, 1998).

[d] All 16-PAH are not included in the 16-PAH factor for every source category; in some cases, there is not a complete set of factors for all 16-PAH since the available test data did not report or sample for a specific PAH compound(s). Refer to the documentation for the Section 116(c)(6) inventory development for a listing of the specific compounds included in the 16-PAH emission factor for a particular source category (U.S. EPA, 1998).

[e] The 7-PAH and 16-PAH emission factors presented here for this source category were not derived from the individual POM emission factors presented earlier in this document for this source category. The factors presented here were developed by EPA from alternative reference sources as part of the national inventory prepared to support the Section 112(c)(6) strategy development. The reader should refer to the documentation for the Section 112(c)(6) inventory development for more information on derivation of 7-PAH and 16-PAH emission factors for this source (U.S. EPA, 1998).

APPENDIX A REFERENCES

U.S. Environmental Protection Agency. 1990 Emissions Inventory of Section 112(c)(6) Pollutants: Polycyclic Organic Matter (POM), 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD)/ 2,3,7,8-Tetrachlorodibenzofuran (TCDF), Polychlorinated Biphenyl Compounds (PCBs), Hexachlorobenzene, Mercury, and Alkylated Lead. Emission Factor and Inventory Group, Research Triangle Park, North Carolina. Final Report. April, 1998.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-454/R-98-014

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
Locating and Estimating Air Emissions From
Sources of Polycyclic Organic Matter

5. REPORT DATE July 1998

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Eastern Research Group, Inc.
1600 Perimeter Park
Morrisville, North Carolina 27560

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-D7-0068

12. SPONSORING AGENCY NAME AND ADDRESS
Emission Monitoring and Analysis Division
OAR, OAQPS, EMAD, EFIG (MD-14)
Emission Factor and Inventory Group
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
EPA Project Officer: Anne A. Pope

16. ABSTRACT

To assist groups interested in inventorying air emissions of various potentially hazardous air pollutants, the EPA is preparing a series of documents such as this to compile available information on sources and emission of these substances. This document deals specifically with polycyclic organic matter. Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of polycyclic organic matter and in making estimates of air emissions therefrom.

This document presents information on (1) the types of sources that may emit polycyclic organic matter, (2) process variations and release points that may be emitted within these sources, and (3) available emissions information indicating the potential for polycyclic organic matter releases into the air from each operation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Polycyclic organic matter (POM) Polyaromatic hydrocarbon compounds (PAH) Air Emissions Sources Locating Air Emissions Sources Hazardous air pollutants		

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 682
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE