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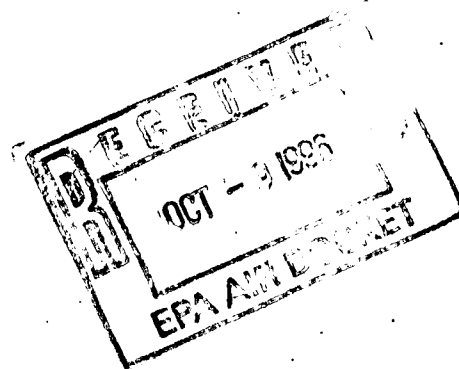
AIR POLLUTANT

EMISSION FACTORS

VOLUME I:

STATIONARY POINT

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7.3 PRIMARY COPPER SMELTING

7.3.1 Process Description¹⁻³

In the United States, copper is produced from sulfide ore concentrates, principally by pyrometallurgical smelting methods. Because the ores usually contain less than 1 percent copper, they must be concentrated before transport to smelters. Concentrations of 15 to 35 percent copper are accomplished at the mine site by crushing, grinding and flotation. Sulfur content of the concentrate ranges from 25 to 35, percent and most of the remainder is iron (25 percent) and water (10 percent). Some concentrates also contain significant quantities of arsenic, cadmium, lead, antimony, and other heavy metals.

A conventional pyrometallurgical copper smelting process is illustrated in Figure 7.3-1. The process includes roasting of ore concentrates to produce calcine, smelting of roasted (calcine feed) or unroasted (green feed) ore concentrates to produce matte, and converting of the matte to yield blister copper product (about 99 percent pure). Typically, the blister copper is fire refined in an anode furnace, cast into "anodes" and sent to an electrolytic refinery for further impurity elimination.

In roasting, charge material of copper concentrate mixed with a siliceous flux (often a low grade ore) is heated in air to about 650°C (1200°F), eliminating 20 to 50 percent of the sulfur as sulfur dioxide (SO₂). Portions of such impurities as antimony, arsenic and lead are driven off, and some iron is converted to oxide. The roasted product, calcine, serves as a dried and heated charge for the smelting furnace. Either multiple hearth or fluidized bed roasters are used for roasting copper concentrate. Multiple hearth roasters accept moist concentrate, whereas fluid bed roasters are fed finely ground material (60 percent minus 200 mesh). With both of these types, the roasting is autogenous. Because there is less air dilution, higher SO₂ concentrations are present in fluidized bed roaster gases than in multiple hearth roaster gases.

In the smelting process, either hot calcines from the roaster or raw unroasted concentrate is melted with siliceous flux in a smelting furnace to produce copper matte, a molten mixture of cuprous sulfide (Cu₂S), ferrous sulfide (FeS) and some heavy metals. The required heat comes from partial oxidation of the sulfide charge and from burning external fuel. Most of the iron and some of the impurities in the charge oxidize with the fluxes to form atop the molten bath a slag, which is periodically removed and discarded. Copper matte remains in the furnace until tapped. Mattes produced by the domestic industry range from 35 to 65 percent copper, with 45 percent the most common. The copper content percentage is referred to as the matte grade. Currently, five smelting furnace technologies are used in the U. S., reverberatory, electric, Noranda, Outokumpu (flash), and Inco (flash).

Reverberatory furnace operation is a continuous process, with frequent charging of input materials and periodic tapping of matte and skimming of slag.

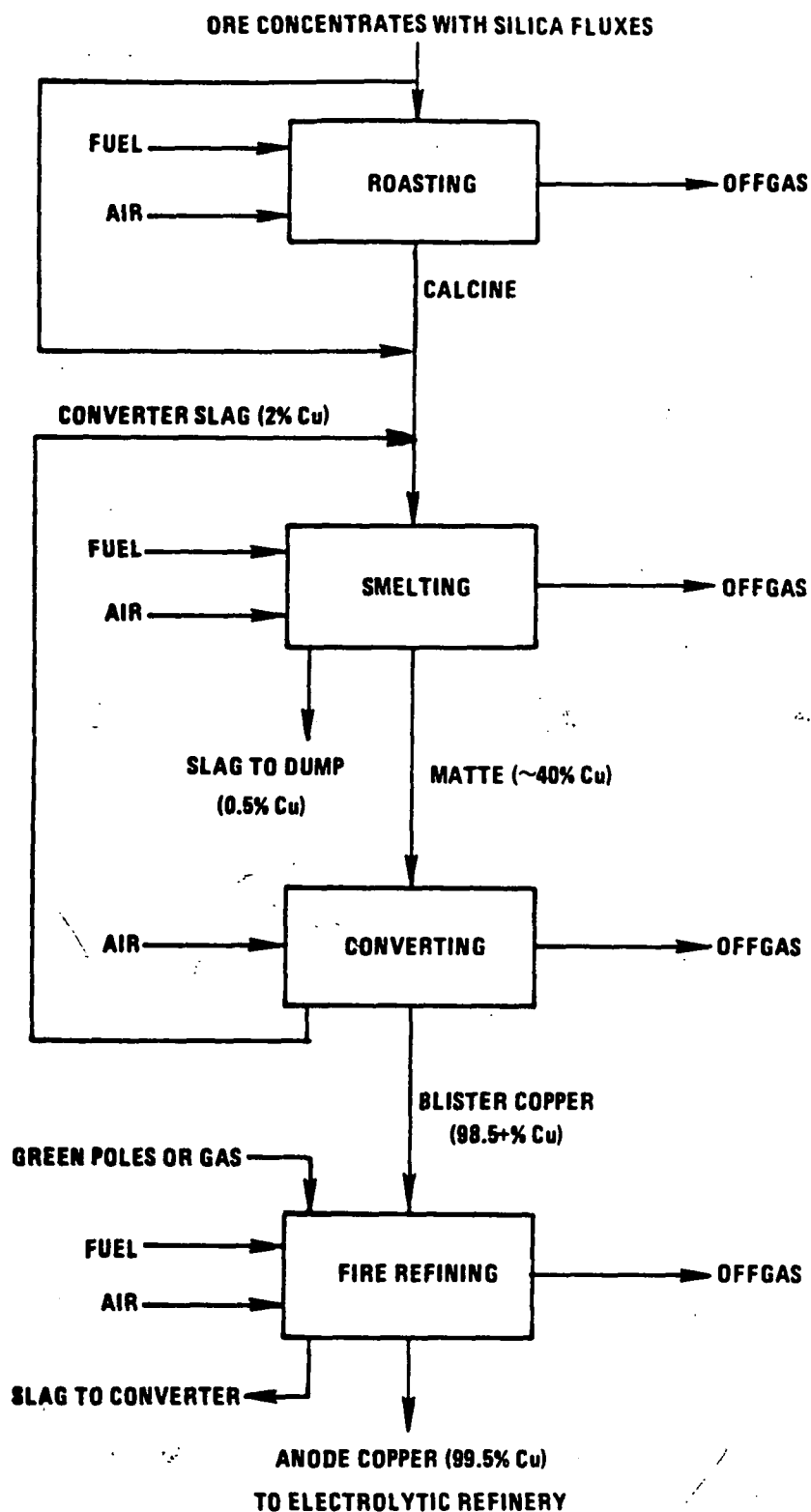


Figure 7.3-1. Typical primary copper smelter process.

1300 tons) of charge per day. Heat is supplied by combustion of oil, gas or pulverized coal, and furnace temperature may exceed 1500°C (2730°F).

For smelting in electric arc furnaces, heat is generated by the flow of an electric current in carbon electrodes lowered through the furnace roof and submerged in the slag layer of the molten bath. The feed generally consists of dried concentrates or calcines, and charging wet concentrates is avoided. The chemical and physical changes occurring in the molten bath are similar to those occurring in the molten bath of a reverberatory furnace. Also, the matte and slag tapping practices are similar at both furnaces. Electric furnaces do not produce fuel combustion gases, so flow rates are lower and SO₂ concentrations higher in the effluent gas than in that of reverberatory furnaces.

Flash furnace smelting combines the operations of roasting and smelting to produce a high grade copper matte from concentrates and flux. In flash smelting, dried ore concentrates and finely ground fluxes are injected, together with oxygen, preheated air, or a mixture of both, into a furnace of special design, where temperature is maintained at approximately 1000°C (1830°F). Flash furnaces, in contrast to reverberatory and electric furnaces, use the heat generated from partial oxidation of their sulfide charge to provide much or all of the energy (heat) required for smelting. They also produce offgas streams containing high concentrations of SO₂.

Slag produced by flash furnace operations contains significantly higher amounts of copper than does that from reverberatory or electric furnace operations. As a result, the flash furnace and converter slags are treated in a slag cleaning furnace to recover the copper. Slag cleaning furnaces usually are small electric furnaces. The flash furnace and converter slags are charged to a slag cleaning furnace and are allowed to settle under reducing conditions, with the addition of coke or iron sulfide. The copper, which is in oxide form in the slag, is converted to copper sulfide, is subsequently removed from the furnace and is charged to a converter with regular matte. If the slag's copper content is low, the slag is discarded.

The Noranda process, as originally designed, allowed the continuous production of blister copper in a single vessel by effectively combining roasting, smelting and converting into one operation. Metallurgical problems, however, led to the operation of these reactors for the production of copper matte. As in flash smelting, the Noranda process takes advantage of the heat energy available from the copper ore. The remaining thermal energy required is supplied by oil burners, or by coal mixed with the ore concentrates.

The final step in the production of blister copper is converting, with the purposes of eliminating the remaining iron and sulfur present in the matte and leaving molten "blister" copper. All but one U. S. smelter uses Pierce-Smith converters, which are refractory lined cylindrical steel shells mounted on trunnions at either end, and rotated about the major axis for charging and pouring. An opening in the center of the converter functions as a mouth through which molten matte, siliceous flux, and scrap copper are charged and gaseous products are vented. Air or oxygen rich air is blown through the molten matte. Iron sulfide (FeS) is oxidized to iron oxide (FeO) and SO₂, and the FeO blowing and slag skimming are repeated until an adequate amount of relatively pure Cu₂S, called "white metal", accumulates in the bottom of the converter. A renewed air blast oxidizes the copper sulfide sulfur to SO₂, leaving blister copper in the

converter. The blister copper is subsequently removed and transferred to refining facilities. This segment of converter operation is termed the finish blow. The SO_2 produced throughout the operation is vented to pollution control devices.

One domestic smelter uses Hoboken converters, the primary advantage of which lies in emission control. The Hoboken converter is essentially like a conventional Pierce-Smith converter, except that this vessel is fitted with a side flue at one end shaped as an inverted U. This flue arrangement permits siphoning of gases from the interior of the converter directly to the offgas collection system, leaving the converter mouth under a slight vacuum.

Blister copper usually contains from 98.5 to 99.5 percent pure copper. Impurities may include gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, tellurium, and zinc. To purify blister copper further, fire refining and electrolytic refining are used. In fire refining, blister copper is placed in a fire refining furnace, a flux is usually added, and air is blown through the molten mixture to oxidize remaining impurities, which are removed as a slag. The remaining metal bath is subjected to a reducing atmosphere to reconvert cuprous oxide to copper. Temperature in the furnace is around 1100°C (2010°F). The fire refined copper is cast into anodes, after which, further electrolytic refining separates copper from impurities by electrolysis in a solution containing copper sulfate and sulfuric acid. Metallic impurities precipitate from the solution and form a sludge that is removed and treated to recover precious metals. Copper is dissolved from the anode and deposited at the cathode. Cathode copper is remelted and made into bars, ingots or slabs for marketing purpose. The copper produced is 99.95 to 99.97 percent pure.

7.3.2 Emissions And Controls

Particulate matter and sulfur dioxide are the principal air contaminants emitted by primary copper smelters. These emissions are generated directly from the processes involved, as in the liberation of SO_2 from copper concentrate during roasting, or in the volatilization of trace elements as oxide fumes. Fugitive emissions are generated by leaks from major equipment during material handling operations.

Roasters, smelting furnaces and converters are sources of both particulate matter and sulfur oxides. Copper and iron oxides are the primary constituents of the particulate matter, but other oxides, such as arsenic, antimony, cadmium, lead, mercury and zinc, may also be present, with metallic sulfates and sulfuric acid mist. Fuel combustion products also contribute to the particulate emissions from multiple hearth roasters and reverberatory furnaces.

Single stage electrostatic precipitators (ESP) are widely used in the primary copper industry to control particulate emissions from roasters, smelting furnaces and converters. Many of the existing ESPs are operated at elevated temperatures, usually from 200° to 340°C (400° to 650°F) and are termed "hot ESPs". If properly designed and operated, these ESPs remove 99 percent or more of the condensed particulate matter present in gaseous effluents. However, at these elevated temperatures, a significant amount of volatile emissions such as arsenic trioxide (As_2O_3) and sulfuric acid mist is present as vapor in the gaseous effluent and thus can not be collected by the particulate control

device at elevated temperatures. At these temperatures, the arsenic trioxide in the vapor state will pass through an ESP. Therefore, the gas stream to be treated must be cooled sufficiently to assure that most of the arsenic present is condensed before entering the control device for collection. At some smelters, the gas effluents are cooled to about 120°C (250°F) temperature before entering a particulate control system, usually an ordinary ("cold") ESP. Spray chambers or air infiltration are used for gas cooling. Fabric filters can also be used for particulate matter collection.

Gas effluents from roasters usually are sent to an ESP or spray chamber/ESP system or are combined with smelter furnace gas effluents before particulate collection. Overall, the hot ESPs remove only 20 to 80 percent of the total particulate (condensed and vapor) present in the gas. Cold ESPs may remove more than 95 percent of the total particulate present in the gas. Particulate collection systems for smelting furnaces are similar to those for roasters. Reverberatory furnace offgases are usually routed through waste heat boilers and low velocity balloon flues to recover large particles and heat, then are routed through an ESP or spray chamber/ESP system.

In the standard Pierce-Smith converter, flue gases are captured during the blowing phase by the primary hood over the converter mouth. To prevent the hood's binding to the converter with splashing molten metal, there is a gap between the hood and the vessel. During charging and pouring operations, significant fugitives may be emitted when the hood is removed to allow crane access. Converter offgases are treated in ESPs to remove particulate matter and in sulfuric acid plants to remove SO₂.

Remaining smelter processes handle material that contains very little sulfur, hence SO₂ emissions from these processes are relatively insignificant. Particulate emissions from fire refining operations, however, may be of concern. Electrolytic refining does not produce emissions unless the associated sulfuric acid tanks are open to the atmosphere. Crushing and grinding systems used in ore, flux and slag processing also contribute to fugitive dust problems.

Control of SO₂ emissions from smelter sources is most commonly performed in a single or double contact sulfuric acid plant. Use of a sulfuric acid plant to treat copper smelter effluent gas streams requires that gas be free from particulate matter and that a certain minimum SO₂ concentration be maintained. Practical limitations have usually restricted sulfuric acid plant application to gas streams that contain at least 3 percent SO₂. Table 7-3-1 shows typical average SO₂ concentrations for the various smelter unit offgases. Currently, converter gas effluents at most smelters are treated for SO₂ control in sulfuric acid plants. Gas effluents of some multiple hearth roaster operations and of all fluid bed roaster operations also are treated in sulfuric acid plants. The weak SO₂ content gas effluents from reverberatory furnace operations are usually released to the atmosphere with no reduction of SO₂. The gas effluents from the other types of smelter furnaces, because of their higher contents of SO₂, are treated in sulfuric acid plants before being vented. Typically, single contact acid plants achieve 92.5 to 98 percent conversion of SO₂ to acid, with approximately 2000 parts per million SO₂ remaining in the acid plant effluent gas. Double contact acid plants collect from 98 to more than 99 percent of the SO₂ and emit about 500 parts per million SO₂. Absorption of the SO₂ in dimethylaniline (DMA) solution has also been used in U. S. smelters to produce liquid SO₂.

TABLE 7.3-1. TYPICAL SULFUR DIOXIDE CONCENTRATIONS
IN OFFGASES FROM PRIMARY COPPER
SMELTING SOURCES

Unit	SO ₂ concentration (volume %)
Multiple hearth roaster	1.5 to 3
Fluidized bed roaster	10 to 12
Reverberatory furnace	0.5 to 1.5
Electric arc furnace	4 to 8
Flash smelting furnace	10 to 70
Continuous smelting furnace	5 to 15
Pierce-Smith converter	4 to 7
Hoboken converter	8
Single contact H ₂ SO ₄ plant	0.2 to 0.26
Double contact H ₂ SO ₄ plant	0.05

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

Actual emissions from a particular smelter unit depend upon the configuration of equipment in that smelting plant and its operating parameters. Table 7.3-2 gives the emission factors for various smelter configurations, and Tables 7.3-3 through 7.3-5 and Figures 7.3-2 through 7.3-4 give size specific emission factors for those copper production processes, where information is available.

7.3.3 Fugitive Emissions

The process sources of particulate matter and SO₂ emission are also the potential fugitive sources of these emissions: roasting, smelting, converting, fire refining and slag cleaning. Table 7.3-6 presents the potential fugitive emission factors for these sources, while Tables 7.3-7 through 7.3-9 and Figures 7.3-5 through 7.3-7 present cumulative size specific particulate emission factors for fugitive emissions from reverberatory furnace matte, slag tapping, converter slag, and copper blow operations. The actual quantities of emissions from these sources depend on the type and condition of the equipment and on the smelter operating techniques. Although emissions from many of these sources are released inside a building, ultimately they are discharged to the atmosphere.

TABLE 7.3-2. EMISSION FACTORS FOR PRIMARY COPPER SMELTERS^{a,b}

EMISSION FACTOR RATING: B

Configuration ^c	By unit	Particulate		Sulfur dioxide ^d		References
		kg/Mg	lb/ton	kg/Mg	lb/ton	
Reverberatory furnace (RF)	RF	25	50	160	320	4-10,
followed by converters (C)	C	18	36	370	740	9,11-15
Multiple hearth roaster (MHR)	MHR	22	45	140	280	4-5,16-17
followed by reverberatory	RF	25	50	90	180	4-9,18-19
furnace (RF) and converters (C)	C	18	36	300	600	8,11-13
Fluid bed roaster (FBR) followed	FBR	NA	NA	180	360	20
by reverberatory furnace (RF)	RF	25	50	90	160	e
and converters (C)	C	18	36	270	540	e
Concentrate dryer (CD) followed	CD	5	10	0.5	1	21-22
by electric furnace (EF) and	EF	50	100	120	240	15
converters (C)	C	18	36	410	820	8,11-13,15
Fluid bed roaster (FBR) followed	FBR	NA	NA	180	360	20
by electric furnace (EF) and	EF	50	100	45	90	15,23
converters (C)	C	18	36	300	600	e
Concentrate dryer (DC) followed	CD	5	10	0.5	1	21-22
by flash furnace (FF),	FF	70	140	410	820	24
cleaning furnace (SS) and	SS ^f	5	10	0.5	1	22
converters (C)	C ^e	NA ^g	NA ^g	120	240	22
Concentrate dryer (CD) followed	CD	5	10	0.5	1	21-22
by Noranda reactors (NR) and	NR	NA	NA	NA	NA	
converters (C)	C	NA	NA	NA	NA	

^aExpressed as units/unit weight of concentrated ore processed by the smelter. Approximately 4 unit weights of concentrate are required to produce 1 unit weight of blister copper. NA = not available.

^bFor particulate matter removal, gaseous effluents from roasters, smelting furnaces and converters usually are treated in hot ESPs at 200 to 340°C (400 to 650°F) or in cold ESPs with gases cooled to about 120°C (250°F) before ESP. Particulate emissions from copper smelters contain volatile metallic oxides which remain in vapor form at higher temperatures (120°C or 250°F). Therefore, overall particulate removal in hot ESPs may range 20 to 80% and in cold ESPs may be 99%. Converter gas effluents and, at some smelters, roaster gas effluents are treated in single contact acid plants (SCAP) or double contact acid plants (DCAP) for SO₂ removal. Typical SCAPs are about 96% efficient, and DCAPs are up to 99.8% efficient in SO₂ removal. They also remove over 99% of particulate matter. Noranda and flash furnace offgases are also processed through acid plants and are subject to the same collection efficiencies as cited for converters and some roasters.

^cIn addition to sources indicated, each smelter configuration contains fire refining anode furnaces after the converters. Anode furnaces emit negligible SO₂. No particulate emission data are available for anode furnaces.

^dFactors for all configurations except reverberatory furnace followed by converters have been developed by normalizing test data for several smelters to represent 30% sulfur content in concentrated ore.

^eBased on the test data for the configuration multiple hearth roaster followed by reverberatory furnace and converters.

^fUsed to recover copper from furnace slag and converter slag.

^gSince converters at flash furnace and Noranda furnace smelters treat high copper content matte, converter particulate emissions from flash furnace smelters are expected to be lower than those from conventional smelters with multiple hearth roasters, reverberatory furnace and converters.

TABLE 7.3-3. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR MULTIPLE HEARTH ROASTER AND REVERBERATORY SMELTER OPERATIONS^a

EMISSION FACTOR RATING: D

Particle size ^b (μm)	Cumulative mass % ≤ stated size		Cumulative emission factors			
	Uncontrolled	ESP controlled	Uncontrolled		ESP controlled ^c	
			Kg/Mg	lb/ton	Kg/Mg	lb/ton
15	100	100	47	95	0.47	0.95
10	100	99	47	94	0.47	0.94
5	100	98	47	93	0.46	0.93
2.5	97	84	46	80	0.40	0.80
1.25	66	76	31	72	0.36	0.72
0.625	25	62	12	59	0.29	0.59
Total	100	100	47	95	0.47	0.95

^aReference 25. Expressed as units/unit weight of concentrated ore processed by the smelter.

^bExpressed as aerodynamic equivalent diameter.

^cNominal particulate removal efficiency is 99%.

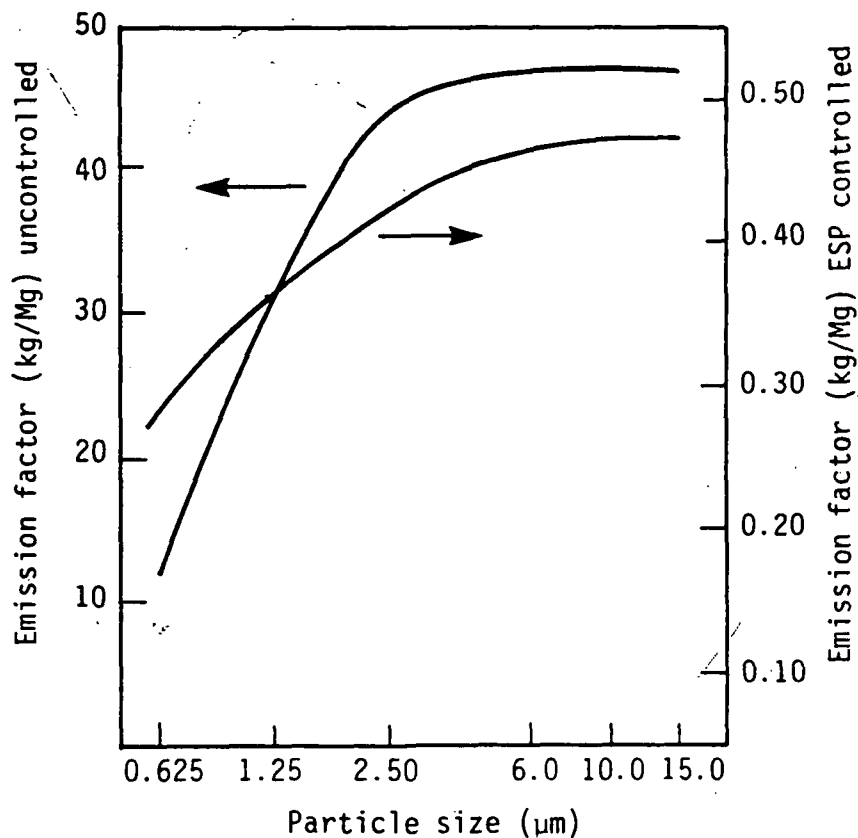


Figure 7.3-2. Size specific emission factors for multiple hearth roaster and reverberatory smelter.

TABLE 7.3-4. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR REVERBERATORY SMELTER OPERATIONS^A

EMISSION FACTOR RATING: E

Particle size ^b (um)	Cumulative mass % ≤ stated size		Cumulative emission factors			
	Uncontrolled	ESP controlled	Uncontrolled		ESP controlled ^c	
			Kg/Mg	lb/ton	Kg/Mg	lb/ton
15	NR	83	NR	NR	0.21	0.42
10	27	78	6.8	13.6	0.20	0.40
5	23	69	5.8	11.6	0.18	0.36
2.5	21	56	5.3	10.6	0.14	0.28
1.25	16	40	4.0	8.0	0.10	0.20
0.625	9	32	2.3	4.6	0.08	0.16
Total	100	100	25	50	0.25	0.50

^aReference 25. Expressed as units/unit weight of concentrated ore processed by the smelter. NR = not reported because of excessive extrapolation.

^bExpressed as aerodynamic equivalent diameter.

^cNominal particulate removal efficiency is 99%.

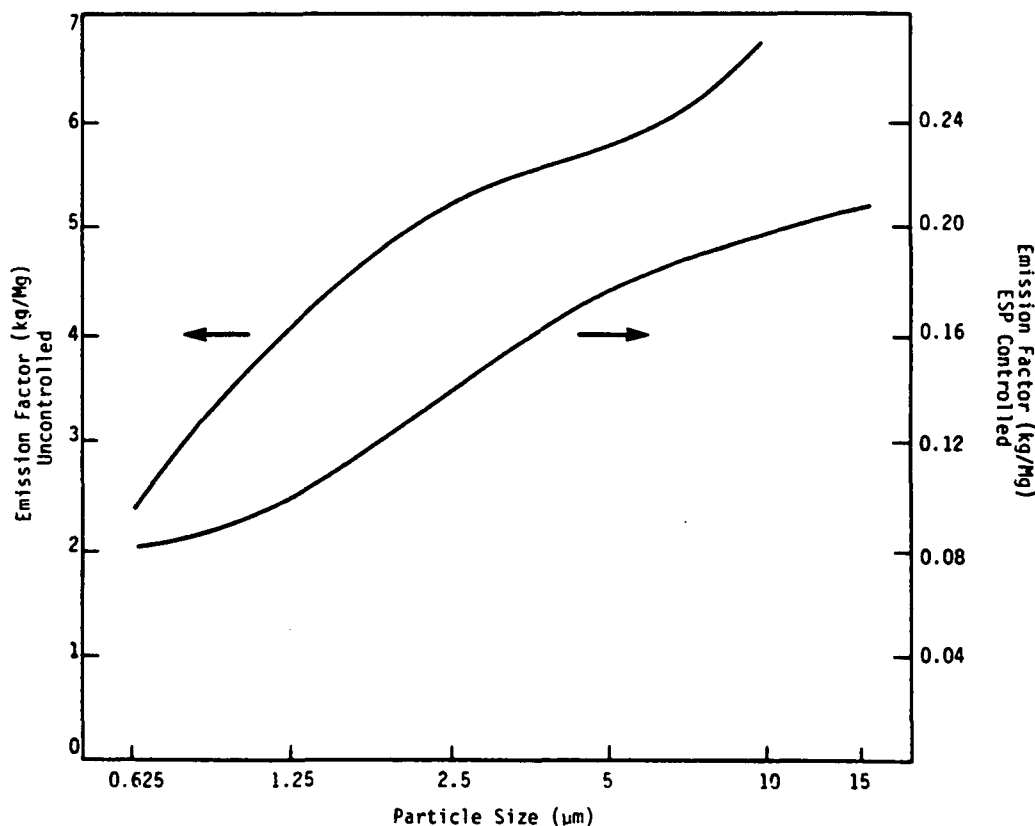


Figure 7.3-3. Size specific emission factors for reverberatory smelting.

TABLE 7.3-5. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR COPPER CONVERTER OPERATIONS^a

EMISSION FACTOR RATING: E

Particle size ^b (um)	Cumulative mass % ≤ stated size		Cumulative emission factors			
	Uncontrolled	ESP controlled	Uncontrolled		ESP controlled ^c	
			Kg/Mg	lb/ton	Kg/Mg	lb/ton
15	NR	100	NR	NR	0.18	0.36
10	59	99	10.6	21.2	0.17	0.36
5	32	72	5.8	11.5	0.13	0.26
2.5	12	56	2.2	4.3	0.10	0.20
1.25	3	42	0.5	1.1	0.08	0.15
0.625	1	30	0.2	0.4	0.05	0.11
Total	100	100	18	36	0.18	0.36

^aReference 25. Expressed as units/unit weight of concentrated ore processed by the smelter. NR = not reported because of excessive extrapolation.

^bExpressed as aerodynamic equivalent diameter.

^cNominal particulate removal efficiency is 99 %.

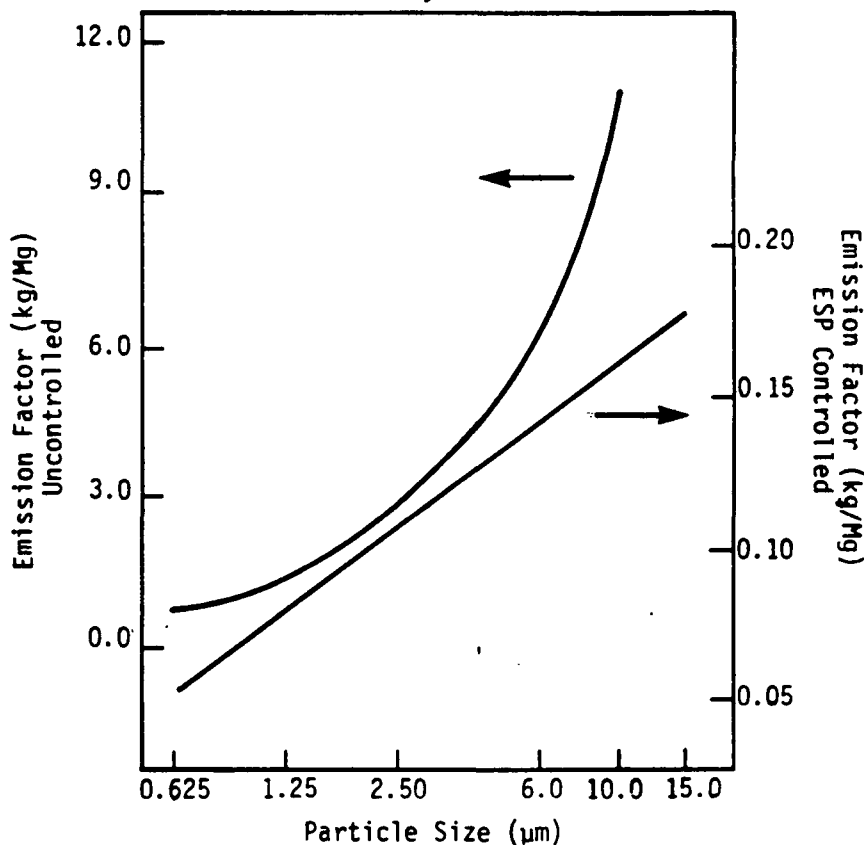


Figure 7.3-4. Size specific emission factors for copper converting.

Fugitive emissions are generated during the discharge and transfer of hot calcine from multiple hearth roasters, with negligible amounts possible from the charging of these roasters. Fluid bed roasting, a closed loop operation, has negligible fugitive emissions.

Matte tapping and slag skimming operations are sources of fugitive emissions from smelting furnaces. Fugitive emissions can also result from charging of a smelting furnace or from leaks, depending upon the furnace type and condition. A typical single matte tapping operation lasts from 5 to 10 minutes and a single slag skimming operation lasts from 10 to 20 minutes. Tapping frequencies vary with furnace capacity and type. In an 8 hour shift, matte is tapped 5 to 20 times, and slag is skimmed 10 to 25 times.

Each of the various stages of converter operation - the charging, blowing, slag skimming, blister pouring, and holding - is a potential source of fugitive emissions. During blowing, the converter mouth is in stack (i. e., a close fitting primary hood is over the mouth to capture offgases). Fugitive emissions escape from the hoods. During charging, skimming and pouring operations, the converter mouth is out of stack (i. e., the converter mouth is rolled out of its vertical position, and the primary hood is isolated). Fugitive emissions are discharged during rollout.

TABLE 7.3-6. FUGITIVE EMISSION FACTORS FOR PRIMARY COPPER SMELTERS^a

EMISSION FACTOR RATING: B

Source of emission	Particulate		SO ₂	
	kg/Mg	lb/ton	kg/Mg	lb/ton
Roaster calcine discharge	1.3	2.6	0.5	1
Smelting furnace ^b	0.2	0.4	2	4
Converter	2.2	4.4	65	130
Converter slag return	NA	NA	0.05	0.1
Anode furnace	0.25	0.5	0.05	0.1
Slag cleaning furnace ^c	4	8	3	6

^aReferences 16,22,25-32. Expressed as mass units/unit weight of concentrated ore processed by the smelter. Approximately 4 unit weights of concentrate are required to produce 1 unit weight of copper metal. Factors for flash furnace smelters and Noranda furnace smelters may be lower than reported values. NA = not available.

^bIncludes fugitive emissions from matte tapping and slag skimming operations. About 50% of fugitive particulate emissions and about 90% of total SO₂ emissions are from matte tapping operations, with remainder from slag skimming.

^cUsed to treat slags from smelting furnaces and converters at the flash furnace smelter.

TABLE 7.3-7. UNCONTROLLED PARTICLE SIZE AND SIZE SPECIFIC EMISSION FACTORS FOR FUGITIVE EMISSIONS FROM REVERBERATORY FURNACE MATTE TAPPING OPERATIONS^a

EMISSION FACTOR RATING: D

Particle size ^b (μm)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	76	0.076	0.152
10	74	0.074	0.148
5	72	0.072	0.144
2.5	69	0.069	0.138
1.25	67	0.067	0.134
0.625	65	0.065	0.130
Total	100	0.100	0.200

^aReference 25. Expressed as units/unit weight of concentrated ore processed by the smelter.

^bExpressed as aerodynamic equivalent diameter.

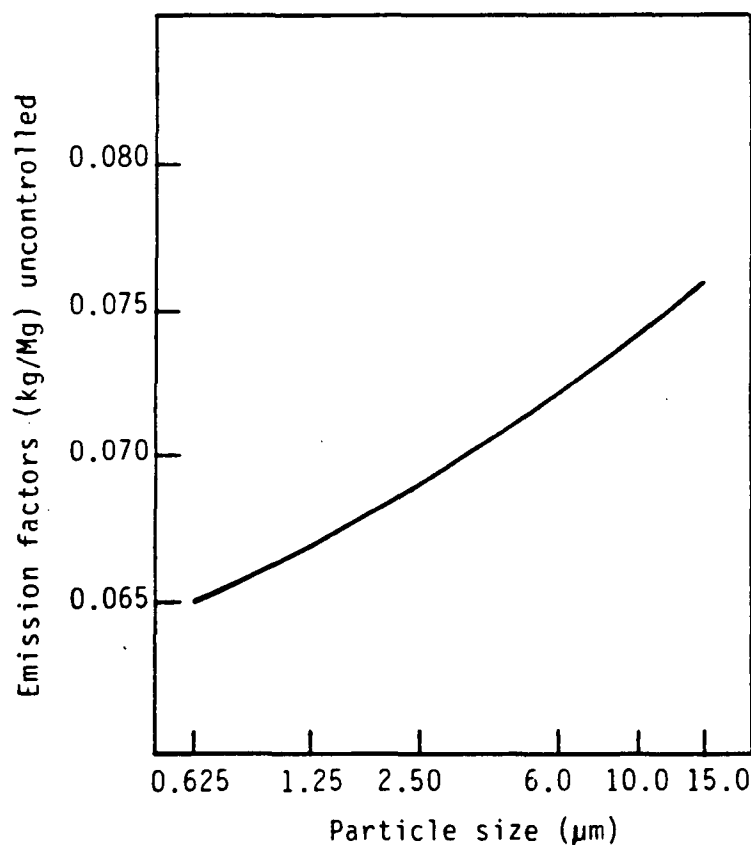


Figure 7.3-5. Size specific fugitive emission factors for reverberatory furnace matte tapping operations.

TABLE 7.3-8. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR FUGITIVE EMISSIONS FROM REVERBERATORY FURNACE SLAG TAPPING OPERATIONS^a

EMISSION FACTOR RATING: D

Particle size ^b (μm)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	33	0.033	0.066
10	28	0.028	0.056
5	25	0.025	0.050
2.5	22	0.022	0.044
1.25	20	0.020	0.040
0.625	17	0.017	0.034
Total	100	0.100	0.200

^aReference 25. Expressed as units/unit weight of concentrated ore processed by the smelter.

^bExpressed as aerodynamic equivalent diameter.

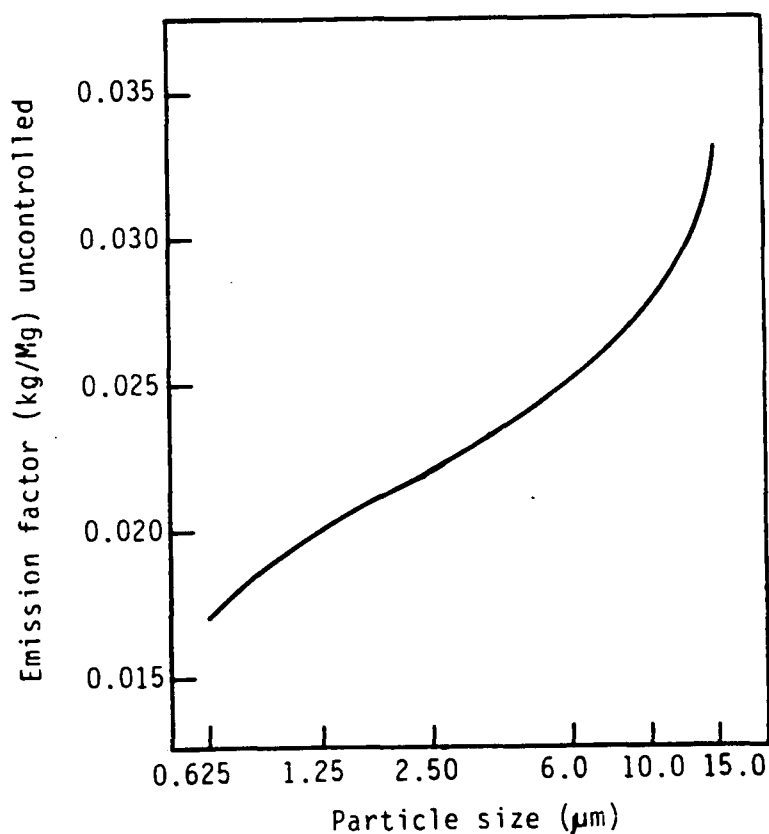


Figure 7.3-6. Size specific fugitive emission factors for reverberatory furnace slag tapping operations.

TABLE 7.3-9. PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR FUGITIVE EMISSIONS FROM CONVERTER SLAG AND COPPER BLOW OPERATIONS^a

EMISSION FACTOR RATING: D

Particle size ^b (μm)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	98	2.2	4.3
10	96	2.1	4.2
5	87	1.9	3.8
2.5	60	1.3	2.6
1.25	47	1.0	2.1
0.625	38	0.8	1.7
Total	100	2.2	4.4

^aReference 25. Expressed as units/unit weight of concentrated ore processed by the smelter.

^bExpressed as aerodynamic equivalent diameter.

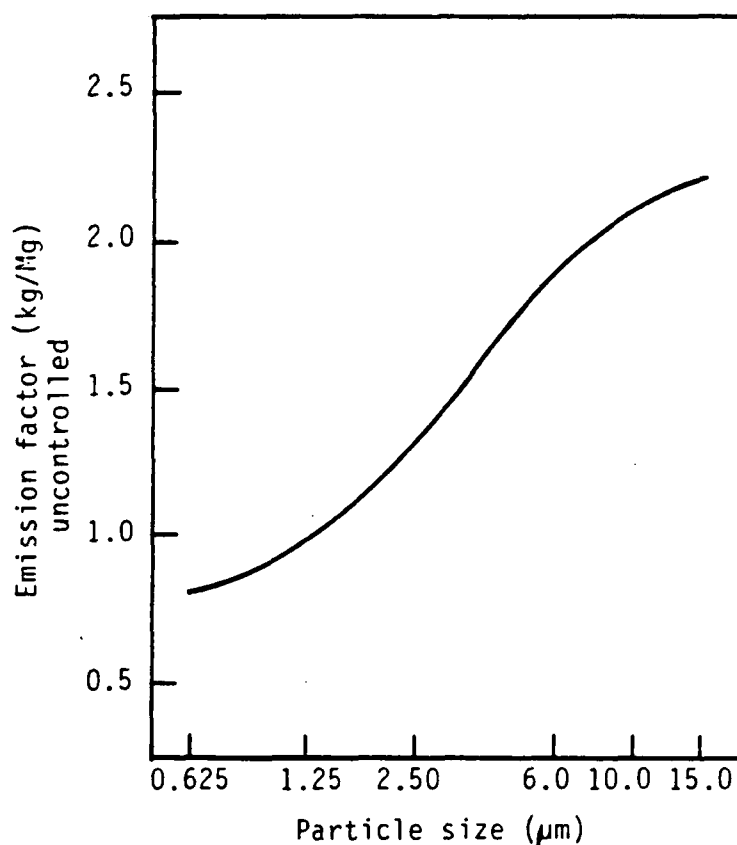


Figure 7.3-7. Size specific fugitive emission factors for converter slag and copper blow operations.

At times during normal smelting operations, slag or blister copper can not be transferred immediately from or to the converters. This condition, holding stage, may occur for several reasons, including insufficient matte in the smelting furnace, the unavailability of a crane, and others. Under these conditions, the converter is rolled out of its vertical position and remains in a holding position and fugitive emissions may result.

7.3.4 Lead Emissions

At primary copper smelters, both process emissions and fugitive particulate from various pieces of equipment contain oxides of many inorganic elements, including lead. The lead content of particulate emissions depends upon both the lead content of the smelter feed and the process offgas temperature. Lead emissions are effectively removed in particulate control systems operating at low temperatures, about 120°C (250°F).

Table 7.3-10 presents process and fugitive lead emission factors for various operations of primary copper smelters.

TABLE 7.3-10. LEAD EMISSION FACTORS FOR PRIMARY COPPER SMELTERS^a

EMISSION FACTOR RATING: C

Operation	Emission factor ^b	
	kg/Mg	lb/ton
Roasting	0.075	0.15
Smelting	0.036	0.072
Converting	0.13	0.27
Refining	NA	NA

^aReference 33. Expressed as units/unit weight of concentrated ore processed by smelter. Approximately four unit weights of concentrate are required to produce one unit weight of copper metal. Based on test data for several smelters with 0.1 to 0.4 % lead in feed throughput. NA = not available.

^bFor process and fugitive emissions totals.

^cBased on test data on multihearth roasters. Includes total of process emissions and calcine transfer fugitive emissions. The latter are about 10% of total process and fugitive emissions.

^dBased on test data on reverberatory furnaces. Includes total process emissions and fugitive emissions from matte tapping and slag skimming operations. Fugitive emissions from matte tapping and slag skimming operations amount to about 35% and 2%, respectively.

^eIncludes total of process and fugitive emissions. Fugitives constitute about 50% of total.

Fugitive emissions from primary copper smelters are captured by applying either local ventilation or general ventilation techniques. Once captured, emissions may be vented directly to a collection device or be combined with process offgases before collection. Close fitting exhaust hood capture systems are used for multiple hearth roasters and hood ventilation systems for smelt matte tapping and slag skimming operations. For converters, secondary hood systems or building evacuation systems are used.

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7.6 PRIMARY LEAD SMELTING

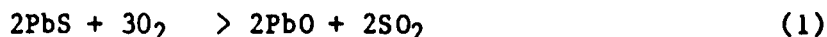
7.6.1 Process Description

Lead is usually found naturally as a sulfide ore containing small amounts of copper, iron, zinc and other trace elements. It is usually concentrated at the mine from an ore of 3 to 8 percent lead to a concentrate of 55 to 70 percent lead, containing from 13 to 19 weight percent free and uncombined sulfur. Processing involves three major steps, sintering, reduction and refining.

A typical diagram of the production of lead metal from ore concentrate, with particle and gaseous emission sources indicated, is shown in Figure 7.6-1.

Sintering - Sinter is produced by a sinter machine, a continuous steel pallet conveyor belt moved by gears and sprockets. Each pallet consists of perforated or slotted grates, beneath which are wind boxes connected to fans to provide a draft, either up or down, through the moving sinter charge. Except for draft direction, all machines are similar in design, construction and operation.

The primary reactions occurring during the sintering process are autogenous, occurring at approximately 1000°C (1800°F):



Operating experience has shown that system operation and product quality are optimum when the sulfur content of the sinter charge is from 5 to 7 weight percent. To maintain this desired sulfur content, sulfide free fluxes such as silica and limestone, plus large amounts of recycled sinter and smelter residues, are added to the mix. The quality of the product sinter is usually determined by its Ritter Index hardness, which is inversely proportional to the sulfur content. Hard quality sinter (low sulfur content) is preferred, because it resists crushing during discharge from the sinter machine. Undersize sinter, usually from insufficient desulfurization, is recycled for further processing.

Of the two kinds of sintering machines, the updraft design is superior for many reasons. First, the sinter bed is more permeable (and hence can be larger), thereby permitting a higher production rate than with a downdraft machine of similar dimensions. Secondly, the small amounts of elemental lead that form during sintering will solidify at their point of formation in updraft machines, but, in downdraft operation, the metal flows down and collects on the grates or at the bottom of the sinter charge, thus causing increased pressure drop and attendant reduced blower capacity. The updraft system also can produce sinter

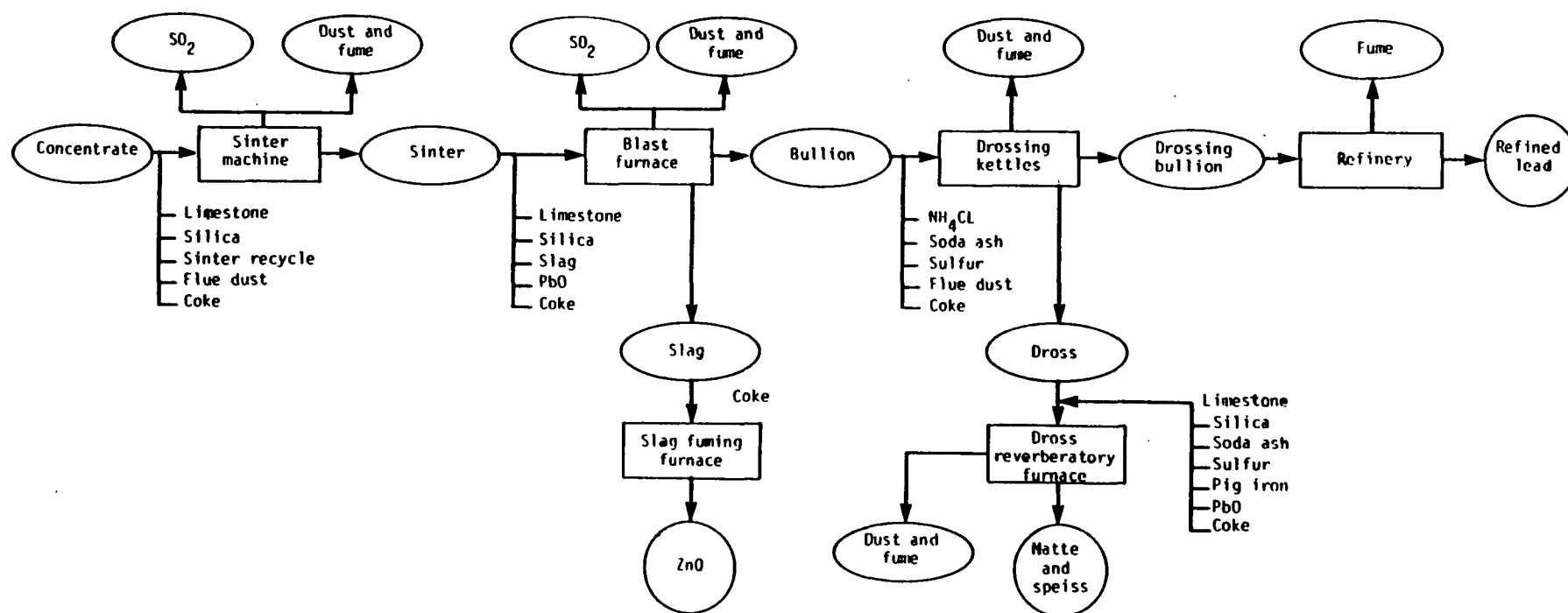
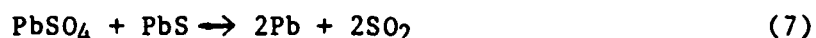


Figure 7.6-1. Typical primary lead processing scheme.

of higher lead content, and it requires less maintenance than the downdraft machine. Finally, and most important from an air pollution control standpoint, updraft sintering can produce a single strong sulfur dioxide (SO₂) effluent stream from the operation, by the use of weak gas recirculation. This permits more efficient and economical use of control methods such as sulfuric acid recovery devices.

Reduction - Lead reduction is carried out in a blast furnace, which basically is a water jacketed shaft furnace supported by a refractory base. Tuyeres, through which combustion air is admitted under pressure, are located near the bottom and are evenly spaced on either side of the furnace.

The furnace is charged with a mixture of sinter (80 to 90 percent of charge), metallurgical coke (8 to 14 percent of charge), and other materials such as limestone, silica, litharge, slag forming constituents, and various recycled and cleanup materials. In the furnace, the sinter is reduced to lead bullion by Reactions 3 through 7.



Carbon monoxide and heat required for reduction are supplied by the combustion of coke. Most of the impurities are eliminated in the slag. Solid products from the blast furnace generally separate into four layers, speiss (the lightest material, basically arsenic and antimony), matte (copper sulfide and other metal sulfides), slag (primarily silicates), and lead bullion. The first three layers are called slag, which is continually collected from the furnace and is either processed at the smelter for its metal content or shipped to treatment facilities.

Sulfur oxides are also generated in blast furnaces from small quantities of residual lead sulfide and lead sulfates in the sinter feed. The quantity of these emissions is a function not only of the sinter's residual sulfur content, but also of the sulfur captured by copper and other impurities in the slag.

Rough lead bullion from the blast furnace usually requires preliminary treatment (drossing) in kettles before undergoing refining operations. First, the bullion is cooled to 370° to 430°C (700 to 800°F). Copper and small amounts of sulfur, arsenic, antimony and nickel collect on the surface as a dross and are removed from the solution. This dross, in turn, is treated in a reverberatory furnace to concentrate the copper and other metal impurities before being routed to copper smelters for their eventual recovery. To enhance copper removal, drossed lead bullion is treated by adding sulfur bearing material, zinc, and/or aluminum, lowering the copper content to approximately 0.01 percent.

Refining - The third and final phase in smelting, the refining of the bullion in cast iron kettles, occurs in five steps:

- Removal of antimony, tin and arsenic
- Removal of precious metals by Parke's Process, in which zinc combines with gold and silver to form an insoluble intermetallic at operating temperatures
- Vacuum removal of zinc
- Removal of bismuth by the Betterson Process, which is the addition of calcium and magnesium to form an insoluble compound with the bismuth that is skimmed from the kettle
- Removal of remaining traces of metal impurities by addition of NaOH and NaNO_3

The final refined lead, commonly from 99.990 to 99.999 percent pure, is then cast into 45 kilogram (100 pound) pigs for shipment.

7.6.2 Emissions And Controls¹⁻²

Each of the three major lead smelting process steps generates substantial quantities of SO_2 and/or particulate.

Nearly 85 percent of the sulfur present in the lead ore concentrate is eliminated in the sintering operation. In handling process offgases, either a single weak stream is taken from the machine hood at less than 2 percent SO_2 , or two streams are taken, a strong stream (5 to 7 percent SO_2) from the feed end of the machine and a weak stream (less than 0.5 percent SO_2) from the discharge end. Single stream operation has been used if there is little or no market for recovered sulfur, so that the uncontrolled, weak SO_2 stream is emitted to the atmosphere. When sulfur removal is required, however, dual stream operation is preferred. The strong stream is sent to a sulfuric acid plant, and the weak stream is vented to the atmosphere after removal of particulate.

When dual gas stream operation is used with updraft sinter machines, the weak gas stream can be recirculated through the bed to mix with the strong gas stream, resulting in a single stream with an SO_2 concentration of about 6 percent. This technique decreases machine production capacity, but it does permit a more convenient and economical recovery of the SO_2 by sulfuric acid plants and other control methods.

Without weak gas recirculation, the end portion of the sinter machine acts as a cooling zone for the sinter and, consequently, assists in the reduction of dust formation during product discharge and screening. However, when recirculation is used, sinter is usually discharged at 400° to 500°C (745° to 950°F), with an attendant increase in particulate. Methods to reduce these dust quantities include recirculating offgases through the sinter bed (to use the bed as a filter) or ducting gases from the sinter machine discharge through a particulate collection device and then to the atmosphere. Because reaction activity has ceased in the discharge area, these gases contain little SO_2 .

Particulate emissions from sinter machines range from 5 to 20 percent of the concentrated ore feed. In product weight, typical emissions are estimated at 106.5 kilograms per megagram (213 pounds per ton) of lead produced. This value and other particulate and SO₂ factors appear in Table 7.6-1.

Typical material balances from domestic lead smelters indicate that about 15 percent of the sulfur in ore concentrate fed to the sinter machine is eliminated in the blast furnace. However, only half of this amount, about 7 percent of the total sulfur in the ore is emitted as SO₂.

The remainder is captured by the slag. The concentration of this SO₂ stream can vary from 1.4 to 7.2 grams per cubic meter (500 to 2500 parts per million) by volume, depending on the amount of dilution air injected to oxidize the carbon monoxide and to cool the stream before baghouse particulate removal.

Particulate emissions from blast furnaces contain many kinds of material, including a range of lead oxides, quartz, limestone, iron pyrites, iron-lime-silicate slag, arsenic and other metallic compounds associated with lead ores. These particles readily agglomerate and are primarily submicron in size, difficult to wet, and cohesive. They will bridge and arch in hoppers. On average, this dust loading is quite substantial, as is shown in Table 7.6-1.

Minor quantities of particulate are generated by ore crushing and materials handling operations, and these emission factors are also presented in Table 7.6-1.

TABLE 7.6-1. UNCONTROLLED EMISSION FACTORS FOR PRIMARY LEAD SMELTING^a

EMISSION FACTOR RATING: B

Process	Total Particulate		Sulfur dioxide		Lead	
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Ore crushing ^b	1.0	2.0	-	-	0.15	0.3
Sintering (updraft) ^c	106.5	213.0	275.0	550.0	87 (4.2-170)	174 (8.4-340)
Blast furnace ^d	180.5	361.0	22.5	45.0	29 (8.7-50)	59 (17.5-100)
Dross reverberatory furnace	10.0	20.0	Neg	Neg	2.4 (1.3-3.5)	4.8 (2.6-7.0)
Materials handling ^f	2.5	5.0	-	-	-	-

^aOre crushing factors expressed as kg/Mg (lb/ton) of crushed ore. All other factors are kg/Mg (lb/ton) of lead product. Dash = no data. Neg = negligible.

^bReferences 2,13.

^cReferences 1, 4-6, 11, 14-17, 21-22.

^dReferences 1-2, 7, 12, 14, 16-17, 19.

^eReferences 2, 11-12, 14, 18, 20.

^fReference 2.

Table 7.6-2 and Figure 7.6-2 present size specific emission factors for the controlled emissions from a primary lead blast furnace. No other size distribution data can be located for point sources within a primary lead processing plant. Lacking definitive data, size distributions for uncontrolled assuming that the uncontrolled size distributions for the sinter machine and blast furnace are the same as for fugitive emissions from these sources.

Tables 7.6-3 through 7.6-7 and Figures 7.6-3 through 7.6-7 present size specific emission factors for the fugitive emissions generated at a primary lead processing plant. The size distribution of fugitive emissions at a primary lead processing plant is fairly uniform, with approximately 79 percent of these emissions at less than 2.5 micrometers. Fugitive emissions less than 0.625 micrometers in size make up approximately half of all fugitive emissions, except from the sinter machine, where they constitute about 73 percent.

Emission factors for total fugitive particulate from primary lead smelting processes are presented in Table 7.6-8. The factors are based on a combination of engineering estimates, test data from plants currently operating, and test data from plants no longer operating. The values should be used with caution, because of the reported difficulty in accurately measuring the source emission rates.

Emission controls on lead smelter operations are for particulate and sulfur dioxide. The most commonly employed high efficiency particulate control devices are fabric filters and electrostatic precipitators (ESP), which often follow centrifugal collectors and tubular coolers (pseudogravity collectors).

Three of the six lead smelters presently operating in the United States use single absorption sulfuric acid plants to control SO₂ emissions from sinter machines and, occasionally, from blast furnaces. Single stage plants can attain sulfur oxide levels of 5.7 grams per cubic meter (2000 parts per million), and dual stage plants can attain levels of 1.6 grams per cubic meter (550 parts per million). Typical efficiencies of dual stage sulfuric acid plants in removing sulfur oxides can exceed 99 percent. Other technically feasible SO₂ control methods are elemental sulfur recovery plants and dimethylaniline (DMA) and ammonia absorption processes. These methods and their representative control efficiencies are given in Table 7.6-9.

TABLE 7.6-2. LEAD EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR BAGHOUSE CONTROLLED BLAST FURNACE FLUE GASES^a

EMISSION FACTOR RATING: C

Particle size ^b (μm)	Cumulative mass % \leq stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	98	1.17	2.34
10	86.3	1.03	2.06
6	71.8	0.86	1.72
2.5	56.7	0.68	1.36
1.25	54.1	0.65	1.29
1.00	53.6	0.64	1.28
0.625	52.9	0.63	1.27
Total	100.0	1.20	2.39

^aReference 9.

^bExpressed as aerodynamic equivalent diameter.

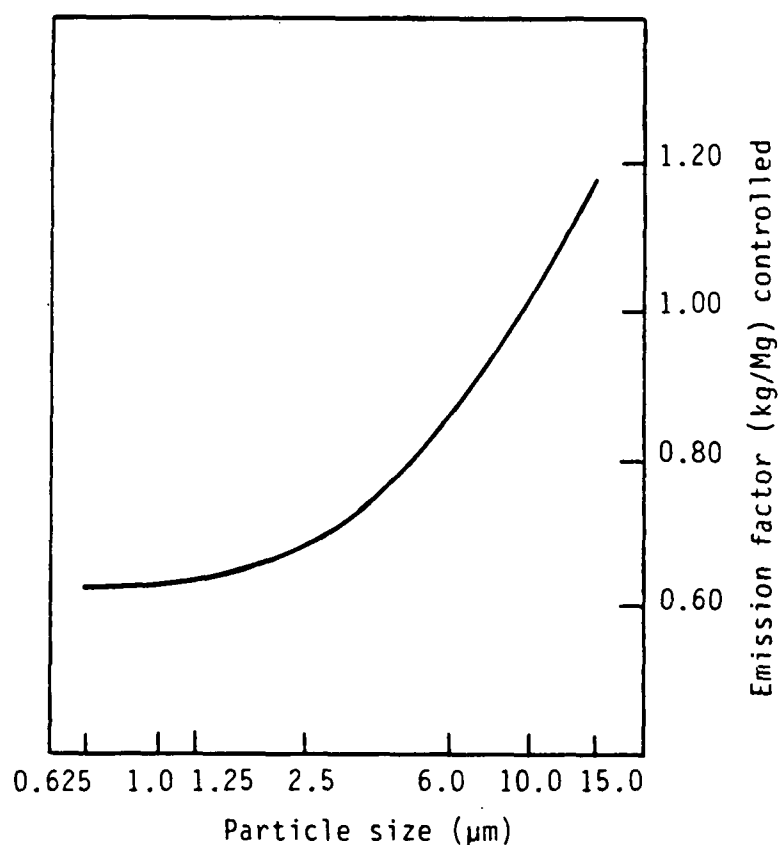


Figure 7.6-2. Size specific emission factors for baghouse controlled blast furnace.

TABLE 7.6-3 UNCONTROLLED FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR LEAD ORE STORAGE^a

EMISSION FACTOR RATING: D

Particle size ^b (μ m)	Cumulative mass % \leq stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	91	0.011	0.023
10	86	0.010	0.021
6	80.5	0.010	0.020
2.5	69.0	0.009	0.017
1.25	61.0	0.008	0.015
1.00	59.0	0.007	0.015
0.625	54.5	0.007	0.013
Total	100.0	0.012	0.025

^aReference 10.

^bExpressed as aerodynamic equivalent diameter.

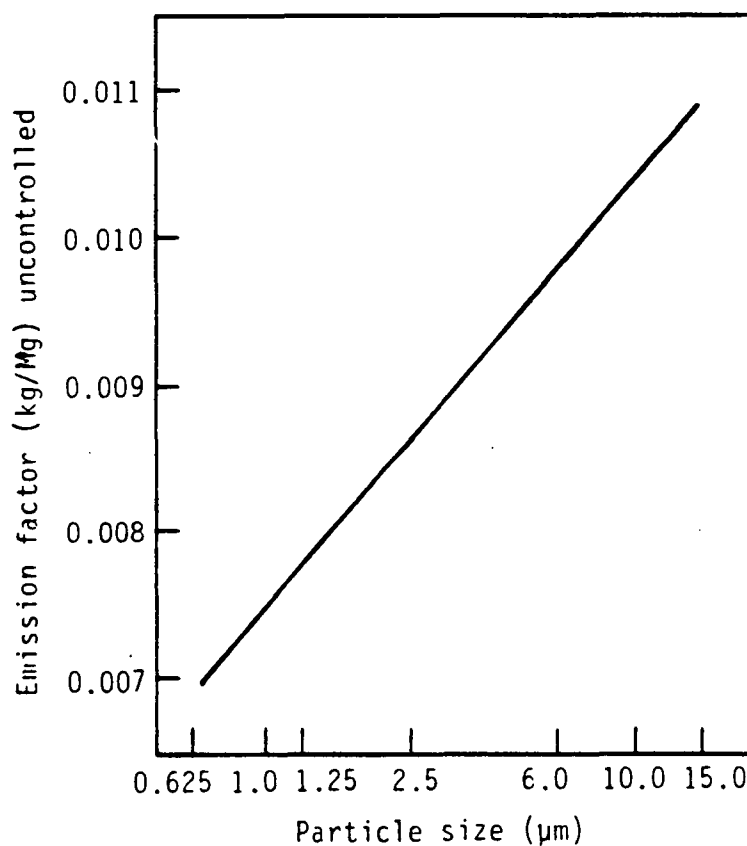


Figure 7.6-3. Size specific uncontrolled fugitive emission factors for lead ore storage.

TABLE 7.6-4. UNCONTROLLED LEAD FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR SINTER MACHINE^a

EMISSION FACTOR RATING: D

Particle size ^b (μm)	Cumulative mass % \leq stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	99	0.10	0.19
10	98	0.10	0.19
6	94.1	0.09	0.17
2.5	87.3	0.08	0.16
1.25	81.1	0.07	0.15
1.00	78.4	0.07	0.15
0.625	73.2	0.07	0.14
Total	100.0	0.10	0.19

^aReference 10.

^bExpressed as aerodynamic equivalent diameter.

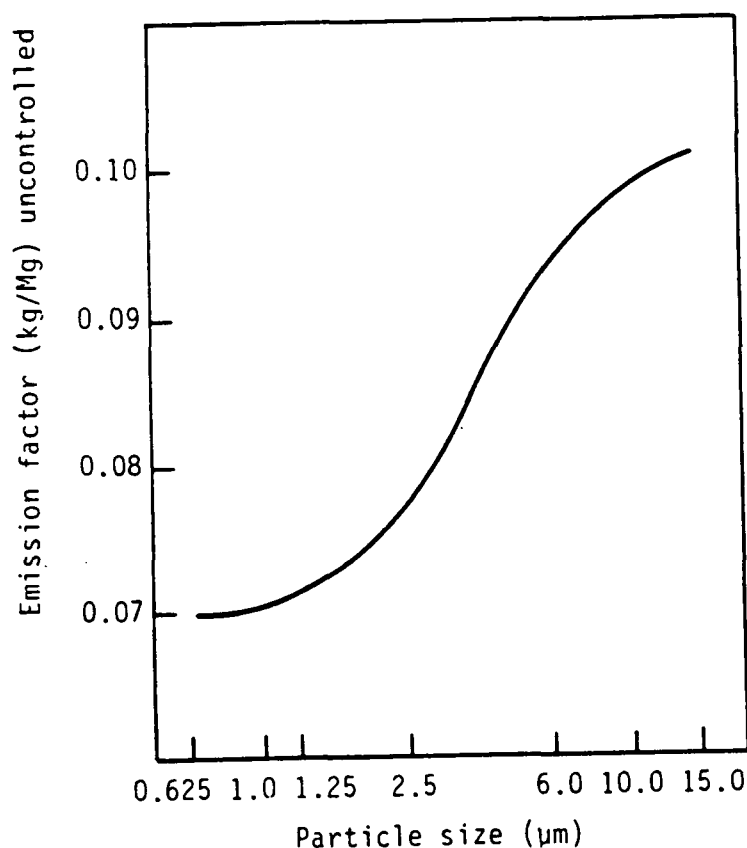


Figure 7.6-4. Size specific fugitive emission factors for uncontrolled sinter machine.

TABLE 7.6-5. UNCONTROLLED LEAD FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR BLAST FURNACE^a

EMISSION FACTOR RATING: D

Particle size ^b (μ m)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	94	0.11	0.23
10	89	0.11	0.21
6	83.5	0.10	0.20
2.5	73.8	0.09	0.17
1.25	65.0	0.08	0.15
1.00	61.8	0.07	0.15
0.625	54.4	0.06	0.13
Total	100.0	0.12	0.24

^aReference 10.

^bExpressed as aerodynamic equivalent diameter.

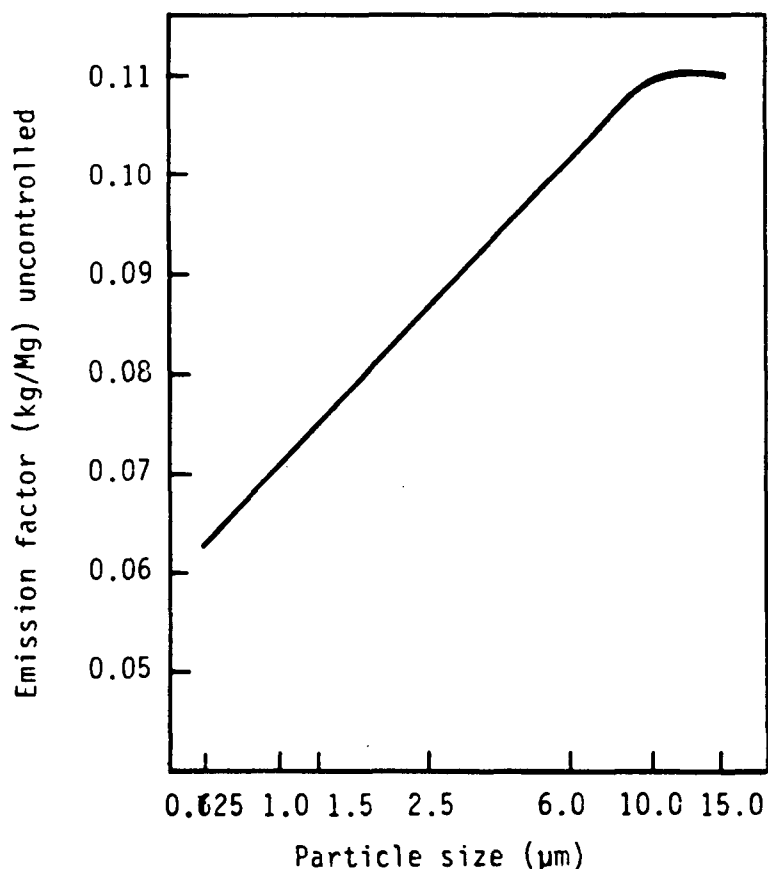


Figure 7.6-5. Size specific lead fugitive emission factors for uncontrolled blast furnace.

TABLE 7.6-6. UNCONTROLLED LEAD FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR DROSS KETTLE^a

EMISSION FACTOR RATING: D

Particle size ^b (μ m)	Cumulative mass % ≤ stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	99	0.18	0.36
10	98	0.18	0.35
6	92.5	0.17	0.33
2.5	83.3	0.15	0.30
1.25	71.3	0.13	0.26
1.00	66.0	0.12	0.24
0.625	51.0	0.09	0.18
Total	100.0	0.18	0.36

^aReference 10.

^bExpressed as aerodynamic equivalent diameter.

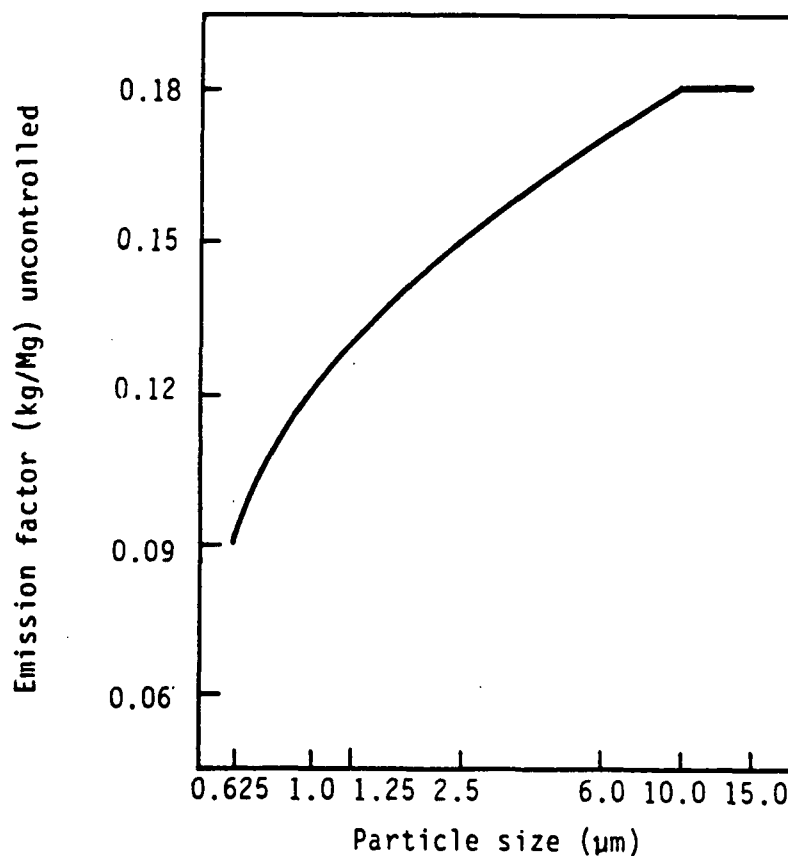


Figure 7.6-6. Size specific lead fugitive emission factors for uncontrolled dross kettle.

TABLE 7.6-7. UNCONTROLLED LEAD FUGITIVE EMISSION FACTORS AND PARTICLE SIZE DISTRIBUTION FOR REVERBERATING FURNACE^a

EMISSION FACTOR RATING: D

Particle size ^b (μm)	Cumulative mass % \leq stated size	Cumulative emission factors	
		kg/Mg	lb/ton
15	99	0.24	0.49
10	98	0.24	0.48
6	92.3	0.22	0.45
2.5	80.8	0.20	0.39
1.25	67.5	0.16	0.33
1.00	61.8	0.15	0.30
0.625	49.3	0.12	0.24
Total	100.0	0.24	0.49

^aReference 10.

^bExpressed as aerodynamic equivalent diameter.

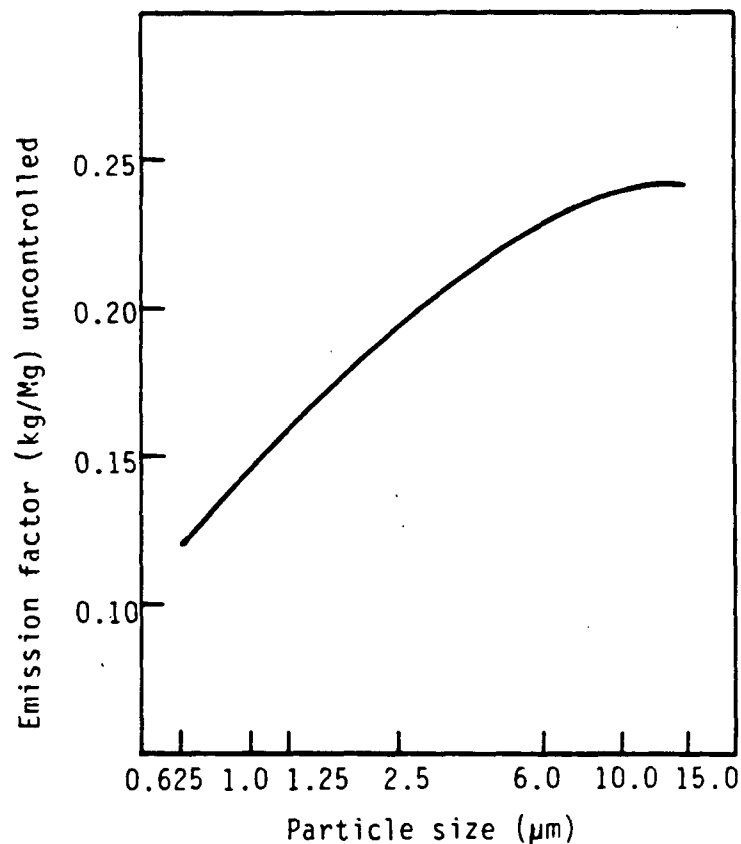


Figure 7.6-7. Size specific lead fugitive emission factors for uncontrolled reverberating furnace.

TABLE 7.6-8. UNCONTROLLED FUGITIVE EMISSION FACTORS FOR
PRIMARY LEAD SMELTING PROCESSES^{a,b}

Emission points	Particulate		Emission Factor Rating
	kg/Mg	lb/ton	
Ore storage ^b	0.012	0.025	D
Ore mixing and pelletizing (crushing)	1.13	2.26	E
Car charging (conveyor loading, transfer) of sinter	0.25	0.50	E
Sinter machine			
Machine leakage ^c	0.34	0.68	E
Sinter return handling	4.50	9.00	E
Machine discharge, sinter crushing, screening ^c	0.75	1.50	E
Sinter transfer to dump area	0.10	0.20	E
Sinter product dump area	0.005	0.01	E
Total building ^b	0.10	0.19	D
Blast furnace			
Lead pouring to ladle, transferring, slag pouring ^c	0.47	0.93	D
Slag cooling ^d	0.24	0.47	E
Zinc fuming furnace vents	2.30	4.60	E
Dross kettle ^b	0.24	0.48	D
Reverberatory furnace leakage ^b	1.50	3.00	D
Silver retort building	0.90	1.80	E
Lead casting	0.44	0.87	E

^aExpressed in units/end product lead produced, except sinter operations, which are units/sinter handled, transferred, charged.

^bReference 10.

^cReferences 12-13. Engineering judgment, using steel sinter machine leakage emission factor.

^dReference 2. Engineering judgment, estimated to be half the magnitude of lead pouring and ladling operations.

TABLE 7.6-9. TYPICAL CONTROL DEVICE EFFICIENCIES IN
PRIMARY LEAD SMELTING OPERATIONS

Control method	Efficiency range (%)	
	Particulate	Sulfur dioxide
Centrifugal collector ^a	80 - 90	NA
Electrostatic precipitator ^a	95 - 99	NA
Fabric filter ^a	95 - 99	NA
Tubular cooler (associated with waste heat boiler) ^a	70 - 80	NA
Sulfuric acid plant (single contact) ^{b,c}	99.5 - 99.9	96 - 97
Sulfuric acid plant (dual contact) ^{b,d}	99.5 - 99.9	96 - 99.9
Elemental sulfur recovery plant ^{b,e}	NA	90
Dimethylaniline (DMA) absorption process ^{b,c}	NA	95 - 99
Ammonia absorption process ^{b,f}	NA	92 - 95

^aReference 2. NA = not available.

^bReference 1.

^cHigh particulate control efficiency from action of acid plant gas cleaning systems. With SO₂ inlet concentrations 5-7%, typical outlet emission levels are 5.7 g/m³ (2000 ppm) for single contact, 1.4 g/m³ (500 ppm) for dual contact.

^dCollection efficiency for a two stage uncontrolled Claus type plant. See Section 5.18, Sulfur Recovery.

^eWith SO₂ inlet concentrations 4-6 %, typical outlet emission levels are from 1.4-8.6 g/m³ (500-3000 ppm).

^fWith SO₂ inlet concentrations of 1.5-2.5 %, typical outlet emission level is 3.4 g/m³ (1200 ppm).

References for Section 7.6

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PETROLEUM INDUSTRY

9.1 PETROLEUM REFINING¹

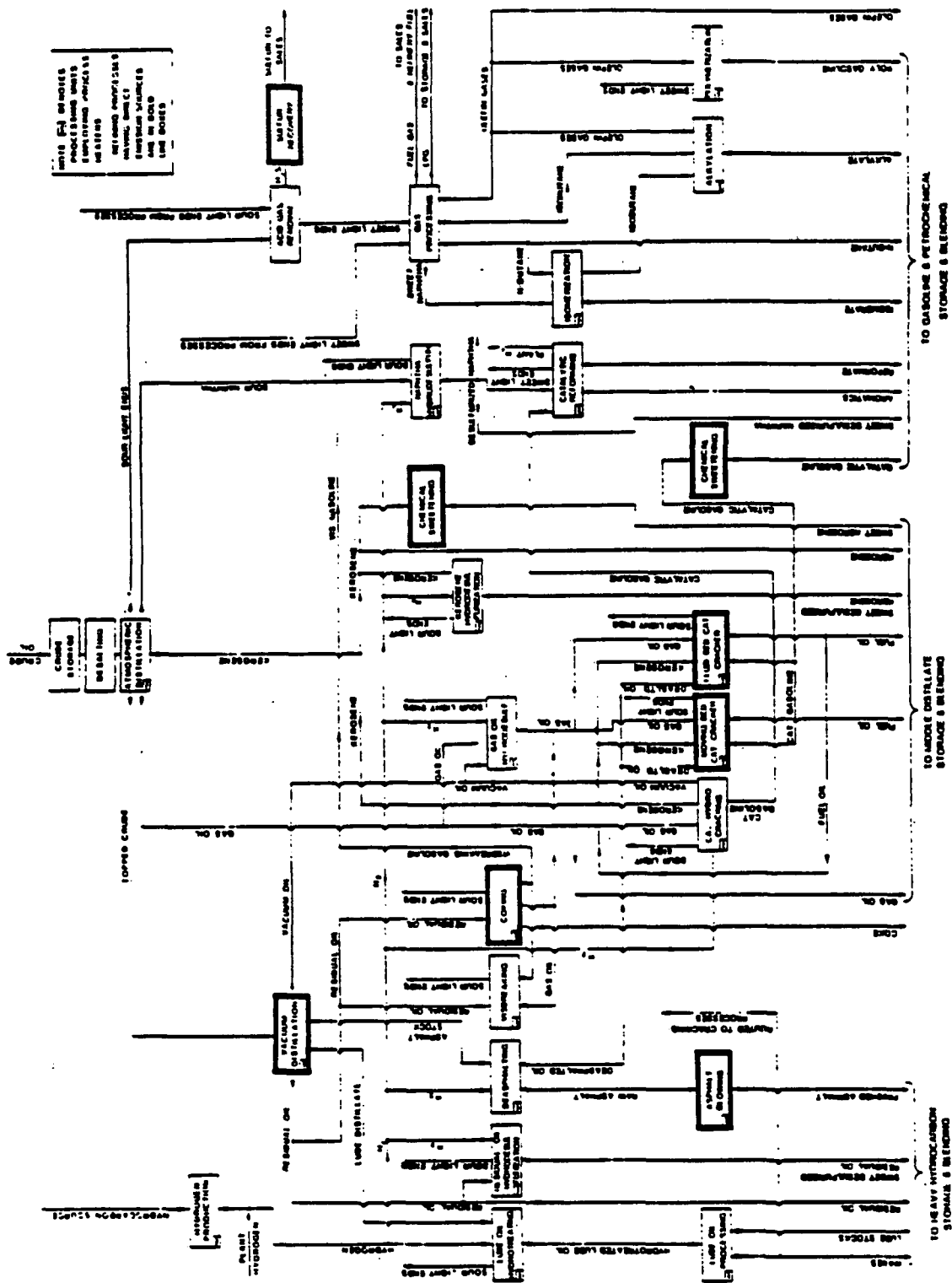
9.1.1 General Description

The petroleum refining industry converts crude oil into more than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petrochemical industry. Petroleum refinery activities start with receipt of crude for storage at the refinery, include all petroleum handling and refining operations, and terminate with storage preparatory to shipping the refined products from the refinery.

The petroleum refining industry employs a wide variety of processes. A refinery's processing flow scheme is largely determined by the composition of the crude oil feedstock and the chosen slate of petroleum products. The example refinery flow scheme presented in Figure 9.1-1 shows the general processing arrangement used by refineries in the United States for major refinery processes. The arrangement of these processes will vary among refineries, and few, if any, employ all of these processes. Petroleum refining processes having direct emission sources are presented in bold-line boxes on the figure.

Listed below are five categories of general refinery processes and associated operations:

1. Separation processes
 - a. atmospheric distillation
 - b. vacuum distillation
 - c. light ends recovery (gas processing)
2. Petroleum conversion processes
 - a. cracking (thermal and catalytic)
 - b. reforming
 - c. alkylation
 - d. polymerization
 - e. isomerization
 - f. coking
 - g. visbreaking
3. Petroleum treating processes
 - a. hydrodesulfurization
 - b. hydrotreating
 - c. chemical sweetening
 - d. acid gas removal
 - e. deasphalting
4. Feedstock and product handling
 - a. storage
 - b. blending
 - c. loading
 - d. unloading
5. Auxiliary facilities
 - a. boilers
 - b. wastewater treatment
 - c. hydrogen production



9.1-1. Schematic of an example integrated petroleum refinery.

- d. sulfur recovery plant
- e. cooling towers
- f. blowdown system
- g. compressor engines

These refinery processes are defined in the following section and their emission characteristics and applicable emission control technology are discussed.

9.1.1.1. Separation Processes—The first phase in petroleum refining operations is the separation of crude oil into its major constituents using three petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery (gas processing). Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons plus small amounts of impurities including sulfur, nitrogen, oxygen, and metals. Refinery separation processes separate these crude oil constituents into common-boiling-point fractions.

9.1.1.2. Conversion Processes—To meet the demands for high-octane gasoline, jet fuel, and diesel fuel, components such as residual oils, fuel oils, and light ends are converted to gasolines and other light fractions. Cracking, coking, and visbreaking processes are used to break large petroleum molecules into smaller petroleum molecules. Polymerization and alkylation processes are used to combine small petroleum molecules into larger ones. Isomerization and reforming processes are applied to rearrange the structure of petroleum molecules to produce higher-value molecules of a similar molecular size.

9.1.1.3. Treating Processes—Petroleum treating processes stabilize and upgrade petroleum products by separating them from less desirable products and by removing objectionable elements. Undesirable elements such as sulfur, nitrogen, and oxygen are removed by hydrodesulfurization, hydrotreating, chemical sweetening and acid gas removal. Treating processes employed primarily for the separation of petroleum products include such processes as deasphalting. Desalting is used to remove salt, minerals, grit, and water from crude oil feed stocks prior to refining. Asphalt blowing is used for polymerizing and stabilizing asphalt to improve its weathering characteristics.

9.1.1.4. Feedstock and Product Handling—The refinery feedstock and product handling operations consist of unloading, storage, blending, and loading activities.

9.1.1.5. Auxiliary Facilities—A wide assortment of processes and equipment not directly involved in the refining of crude oil are used in functions vital to the operation of the refinery. Examples are boilers, wastewater treatment facilities, hydrogen plants, cooling towers, and sulfur recovery units. Products from auxiliary facilities (clean water, steam, and process heat) are required by most refinery process units throughout the refinery.

9.1.2 Process Emission Sources and Control Technology

This section presents descriptions of those refining processes that are significant air pollutant contributors. Process flow schemes, emission characteristics, and emission control technology are discussed for each process. Table 9.1-1 lists the emission factors for direct-process emissions in petroleum refineries. The following process emission sources are discussed in this section on petroleum refining emissions:

1. Vacuum distillation.
2. Catalytic cracking.
3. Thermal cracking processes.
4. Utility boilers.
5. Heaters.

6. Compressor engines.
7. Blowdown systems.
8. Sulfur recovery.

9.1.2.1. Vacuum Distillation—Topped crude withdrawn from the bottom of the atmospheric distillation column is composed of high-boiling-point hydrocarbons. When distilled at atmospheric pressures, the crude oil decomposes and polymerizes to foul equipment. To separate topped crude into components, it must be distilled in a vacuum column at a very low pressure and in a steam atmosphere.

In the vacuum distillation unit, topped crude is heated with a process heater to temperatures ranging from 700 to 800° F (370 to 425° C). The heated topped crude is flashed into a multi-tray vacuum distillation column operating at vacuums ranging from 0.5 to 2 psia (350 to 1400 kg/m²). In the vacuum column, the topped crude is separated into common-boiling-point fractions by vaporization and condensation. Stripping steam is normally injected into the bottom of the vacuum distillation column to assist in the separation by lowering the effective partial pressures of the components. Standard petroleum fractions withdrawn from the vacuum distillation column include lube distillates, vacuum oil, asphalt stocks, and residual oils. The vacuum in the vacuum distillation column is normally maintained by the use of steam ejectors but may be maintained by the use of vacuum pumps.

The major sources of atmospheric emissions from the vacuum distillation column are associated with the steam ejectors or vacuum pumps. A major portion of the vapors withdrawn from the column by the ejectors or pumps are recovered in condensers. Historically, the noncondensable portion of the vapors has been vented to the atmosphere from the condensers. There are approximately 50 pounds (23 kg) of noncondensable hydrocarbons per 1000 barrels of topped crude processed in the vacuum distillation column.^{2,12,13} A second source of atmospheric emissions from vacuum distillation columns is combustion products from the process heater. Process heater requirements for the vacuum distillation column are approximately 37,000 Btu per barrel (245 Joules/cm³) of topped crude processed in the vacuum column. Process heater emissions and their control are discussed later in this section. Fugitive hydrocarbon emissions from leaking seals and fittings are also associated with the vacuum distillation unit, but these are minimized by the low operating pressures and low vapor pressures in the unit. Fugitive emission sources are also discussed later in this section.

Control technology applicable to the noncondensable emissions vented from the vacuum ejectors or pumps include venting into blowdown systems or fuel gas systems, and incineration in furnaces or waste heat boilers.^{2,12,13} These control techniques are generally greater than 99 percent efficient in the control of hydrocarbon emissions, but they also contribute to the emission of combustion products.

9.1.2.2. Catalytic Cracking—Catalytic cracking, using heat, pressure, and catalysts, converts heavy oils into lighter products with product distributions favoring the more valuable gasoline and distillate blending components. Feedstocks are usually gas oils from atmospheric distillation, vacuum distillation, coking, and deasphalting processes. These feedstocks typically have a boiling range of 650 to 1000° F (340 to 540° C). All of the catalytic cracking processes in use today can be classified as either fluidized-bed or moving-bed units.

Fluidized-bed Catalytic Cracking (FCC) — The FCC process uses a catalyst in the form of very fine particles that act as a fluid when aerated with a vapor. Fresh feed is preheated in a process heater and introduced into the bottom of a vertical transfer line or riser with hot regenerated catalyst. The hot catalyst vaporizes the feed bringing both to the desired reaction temperature, 880 to 980° F (470 to 525° C). The high activity of modern catalysts causes most of the cracking reactions to take place in the riser as the catalyst and oil mixture flows upward into the reactor. The hydrocarbon vapors are separated from the catalyst particles by cyclones in the reactor. The reaction products are sent to a fractionator for separation.

The spent catalyst falls to the bottom of the reactor and is steam stripped as it exists the reactor bottom to remove absorbed hydrocarbons. The spent catalyst is then conveyed to a regenerator. In the regenerator, coke deposited on the catalyst as a result of the cracking reactions is burned off in a controlled combustion process with preheated air. Regenerator temperature is usually 1100 to 1250° F (590 to 675° C). The catalyst is then recycled to be mixed with fresh hydrocarbon feed.

Moving-bed Catalytic Cracking (TCC)— In the TCC process, catalyst beads (~0.5 cm) flow by gravity into the top of the reactor where they contact a mixed-phase hydrocarbon feed. Cracking reactions take place as the catalyst and hydrocarbons move concurrently downward through the reactor to a zone where the catalyst is separated from the vapors. The gaseous reaction products flow out of the reactor to the fractionation section of the unit. The catalyst is steam stripped to remove any adsorbed hydrocarbons. It then falls into the regenerator where coke is burned from the catalyst with air. The regenerated catalyst is separated from the flue gases and recycled to be mixed with fresh hydrocarbon feed. The operating temperatures of the reactor and regenerator in the TCC process are comparable to those in the FCC process.

Air emissions from catalytic cracking processes are (1) combustion products from process heaters and (2) flue gas from catalyst regeneration. Emissions from process heaters are discussed later in this section. Emissions from the catalyst regenerator include hydrocarbons, oxides of sulfur, ammonia, aldehydes, oxides of nitrogen, cyanides, carbon monoxide, and particulates (Table 9.1-1). The particulate emissions from FCC units are much greater than those from TCC units because of the higher catalyst circulation rates used.^{2,3,5}

FCC particulate emissions are controlled by cyclones and/or electrostatic precipitators. Particulate control efficiencies are as high as 80 to 85 percent.^{3,5} Carbon monoxide wasteheat boilers reduce the carbon monoxide and hydrocarbon emissions from FCC units to negligible levels.³ TCC catalyst regeneration produces similar pollutants to FCC units but in much smaller quantities (Table 9.1-1). The particulate emissions from a TCC unit are normally controlled by high-efficiency cyclones. Carbon monoxide and hydrocarbon emissions from a TCC unit are incinerated to negligible levels by passing the flue gases through a process heater fire-box or smoke plume burner. In some installations, sulfur oxides are removed by passing the regenerator flue gases through a water or caustic scrubber.^{2,3,5}

9.1.2.3 Thermal Cracking — Thermal cracking processes include visbreaking and coking, which break heavy oil molecules by exposing them to high temperatures.

Visbreaking — Topped crude or vacuum residuals are heated and thermally cracked (850 to 900° F, 50 to 250 psig) (455 to 480° C, 3.5 to 17.6 kg/cm²) in the visbreaker furnace to reduce the viscosity or pour point of the charge. The cracked products are quenched with gas oil and flashed into a fractionator. The vapor overhead from the fractionator is separated into light distillate products. A heavy distillate recovered from the fractionator liquid can be used as a fuel oil blending component or used as catalytic cracking feed.

Coking — Coking is a thermal cracking process used to convert low value residual fuel oil to higher value gas oil and petroleum coke. Vacuum residuals and thermal tars are cracked in the coking process at high temperature and low pressure. Products are petroleum coke, gas oils, and lighter petroleum stocks. Delayed coking is the most widely used process today, but fluid coking is expected to become an important process in the future.

In the delayed coking process, heated charge stock is fed into the bottom section of a fractionator where light ends are stripped from the feed. The stripped feed is then combined with recycle products from the coke drum and rapidly heated in the coking heater to a temperature of 900 to 1100° F (480 to 590° C). Steam injection is used to control the residence time in the heater. The vapor-liquid feed leaves the heater, passing to a coke drum where, with controlled residence time, pressure (25 to 30 psig) (1.8 to 2.1 kg/cm²), and temperature (750° F) (400° C), it is cracked to form coke and vapors. Vapors from the drum return to the fractionator where the thermal cracking products are recovered.

9.1-6

EMISSION FACTORS

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Table 9.1-1. EMISSION FACTORS FOR PETROLEUM REFINERIES

Process	Particulates	Sulfur oxides (as SO ₂)	Carbon monoxide	Total hydrocarbons ^a	Nitrogen oxides (as NO ₂)	Aldehydes	Ammonia	Emission factor rating
Boilers and process heaters.								
Fuel Oil	See Section 1.3 - Fuel Oil Combustion							
Natural Gas	See Section 1.4 - Natural Gas Combustion							
Fluid catalytic cracking units ^b								
Uncontrolled								
lb/10 ³ bbl fresh feed	242 (93 to 340) ^c	493 (100 to 825)	13,700	220	71.0 (37.1 to 145.0)	19	54	B
kg/10 ³ liters fresh feed	0.995 (0.267 to 0.978)	1.413 (0.266 to 1.505)	39.2	0.830	0.204 (0.107 to 0.416)	0.054	0.155	B
Electrostatic precipitator and CO boiler								
lb/10 ³ bbl fresh feed	45 ^d (7 to 150)	493 (100 to 825)	Neg ^e	Neg	71.0 ^f (37.1 to 145.0)	Neg	Neg	B
kg/10 ³ liters fresh feed	0.126 (0.020 to 0.428)	1.413 (0.266 to 1.505)	Neg	Neg	0.204 (0.107 to 0.416)	Neg	Neg	B
Moving-bed catalytic cracking units ^g								
lb/10 ³ bbl fresh feed	17	60	3,800	87	5	12	6	B
kg/10 ³ liters fresh feed	0.049	0.171	10.8	0.250	0.014	0.034	0.017	B
Fluid coking units ^h								
Uncontrolled								
lb/10 ³ bbl fresh feed	523	NA ⁱ	NA	NA	NA	NA	NA	C
kg/10 ³ liters fresh feed	150	NA	NA	NA	NA	NA	NA	C
Electrostatic precipitator and CO boiler								
lb/10 ³ bbl fresh feed	6.85	NA	Neg	Neg	NA	Neg	Neg	C
kg/10 ³ liters fresh feed	0.0196	NA	Neg	Neg	NA	Neg	Neg	C
Delayed coking units	NA	NA	NA	NA	NA	NA	NA	
Compressor engines ^j								
Reciprocating engines								
lb/10 ³ ft ³ gas burned	Neg	2s ^k	0.43	1.4	3.4	0.1	0.2	B
kg/10 ³ m ³ gas burned	Neg	32s	7.02	21.8	55.4	1.61	3.2	B
Gas turbines								
lb/10 ³ ft ³ gas burned	Neg	2s	0.12	0.02	0.3	NA	NA	B
kg/10 ³ m ³ gas burned	Neg	32s	1.94	0.29	4.7	NA	NA	B

(40)

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Petroleum Industry

9.1-7

Table 9.1-1. (Continued) EMISSION FACTORS FOR PETROLEUM REFINERIES

Process	Particulates	Sulfur oxides (as SO ₂)	Carbon monoxide	Total hydrocarbons	Nitrogen oxides (as NO ₂)	Aldehydes	Ammonia	Emission factor rating
Blowdown systems¹								
Uncontrolled								
lb/10 ³ bbl refinery feed	Neg	Neg	Neg	580	Neg	Neg	Neg	C
kg/10 ³ liters refinery feed	Neg	Neg	Neg	1.952	Neg	Neg	Neg	C
Vapor recovery system and flaring								
lb/10 ³ bbl refinery feed	Neg	26.9	4.3	0.8	18.9	Neg	Neg	C
kg/10 ³ liters refinery feed	Neg	0.077	0.012	0.002	0.054	Neg	Neg	C
Vacuum distillation^m								
column condensers								
Uncontrolled								
lb/10 ³ bbl refinery feed	Neg	Neg	Neg	18	Neg	Neg	Neg	C
kg/10 ³ liters refinery feed	Neg	Neg	Neg	0.052	Neg	Neg	Neg	C
lb/10 ³ bbl vacuum feed	Neg	Neg	Neg	50 (0-130)	Neg	Neg	Neg	C
kg/10 ³ liters vacuum feed	Neg	Neg	Neg	0.144	Neg	Neg	Neg	C
Controlled	Neg	Neg	Neg	Neg	Neg	Neg	Neg	C
Claus plant and tail gas treatment		See section 5.18						

^a Overall, less than 1 percent by weight of the total hydrocarbon emissions are methane.

^b References 2 through 8.

^c Numbers in parenthesis indicate range of values observed.

^d Under the New Source Performance Standards, controlled FCC regenerators will have particulate emissions lower than 18 lb/10³ bbl fresh feed.

^e Negligible emission.

^f May be higher due to the combustion of ammonia.

^g Reference 2.

^h Reference 5.

ⁱ NA, Not Available.

^j References 9, 10.

^k s = Refinery gas sulfur content (lb/1000 h³): Factors based on 100 percent combustion of sulfur to SO₂.

^l References 2, 11.

^m References 2, 12, 13.

In the fluid coking process, typified by Flexicoking, residual oil feeds are injected into the reactor where they are thermally cracked, yielding coke and a wide range of vapor products. Vapors leave the reactor and are quenched in a scrubber where entrained coke fines are removed. The vapors are then fractionated. Coke from the reactor enters a heater and is devolatilized. The volatiles from the heater are treated for fines and sulfur removal to yield a particulate free, low-sulfur fuel gas. The devolatilized coke is circulated from the heater to a gasifier where 95 percent of the reactor coke is gasified at high temperature with steam and air or oxygen. The gaseous products and coke from the gasifier are returned to the heater to supply heat for the devolatilization. These gases exit the heater with the heater volatiles through the same fines and sulfur removal processes.

From available literature, it is unclear what emissions are released and where they are released. Air emissions from thermal cracking processes include coke dust from decoking operations, combustion gases from the visbreaking and coking process heaters, and fugitive emissions. Emissions from the process heaters are discussed later in this section. Fugitive emissions from miscellaneous leaks are significant because of the high temperatures involved, and are dependent upon equipment type and configuration, operating conditions, and general maintenance practices. Fugitive emissions are also discussed later in this section. Particulate emissions from delayed coking operations are potentially very significant. These emissions are associated with removing the coke from the coke drum and subsequent handling and storage operations. Hydrocarbon emissions are also associated with cooling and venting the coke drum prior to coke removal. However, comprehensive data for delayed coking emissions have not been included in available literature.^{4,5}

Particulate emission control is accomplished in the decoking operation by wetting down the coke.⁶ Generally, there is no control of hydrocarbon emissions from delayed coking. However, some facilities are now collecting coke drum emissions in an enclosed system and routing them to a refinery flare.^{4,5}

9.1.2.4 Utilities Plant — The utilities plant supplies the steam necessary for the refinery. Although the steam can be used to produce electricity by throttling through a turbine, it is primarily used for heating and separating hydrocarbon streams. When used for heating, the steam usually heats the petroleum indirectly in heat exchangers and returns to the boiler. In direct contact operations, the steam can serve as a stripping medium or a process fluid. Steam may also be used in vacuum ejectors to produce a vacuum. Emissions from boilers and applicable emission control technology are discussed in much greater detail in Chapter 1.0.

9.1.2.5 Sulfur Recovery Plant — Sulfur recovery plants are used in petroleum refineries to convert hydrogen sulfide (H_2S) separated from refinery gas streams into the more disposable by-product, elemental sulfur. Emissions from sulfur recovery plants and their control are discussed in Section 5.18.

9.1.2.6 Blowdown System — The blowdown system provides for the safe disposal of hydrocarbons (vapor and liquid) discharged from pressure relief devices.

Most refining processing units and equipment subject to planned or unplanned hydrocarbon discharges are manifolded into a collection unit, called the blowdown system. By using a series of flash drums and condensers arranged in decreasing pressure, the blowdown is separated into vapor and liquid cuts. The separated liquid is recycled into the refinery. The gaseous cuts can either be smokelessly flared or recycled.

Uncontrolled blowdown emissions primarily consist of hydrocarbons, but can also include any of the other criteria pollutants. The emission rate in a blowdown system is a function of the amount of equipment manifolded into the system, the frequency of equipment discharges, and the blowdown system controls.

Emissions from the blowdown system can be effectively controlled by combustion of the noncondensables in a flare. To obtain complete combustion or smokeless burning (as required by most states), steam is injected in the combustion zone of the flare to provide turbulence and to inspire air. Steam injection also reduces emissions of nitrogen oxides by lowering the flame temperature. Controlled emissions are listed in Table 9.1-1.^{2,11}

9.1.2.7 Process Heaters - Process heaters (furnaces) are used extensively in refineries to supply the heat necessary to raise the temperature of feed materials to reaction or distillation level. They are designed to raise petroleum fluid temperatures to a maximum of about 950°F (510°C). The fuel burned may be refinery gas, natural gas, residual fuel oils, or combinations, depending on economics, operating conditions and emission requirements. Process heaters may also use carbon monoxide-rich regenerator flue gas as fuel.

All the criteria pollutants are emitted from process heaters. The quantity of these emissions is a function of the type of fuel burned, the nature of the contaminants in the fuel, and the heat duty of the furnace. Sulfur oxide can be controlled by fuel desulfurization or flue gas treatment. Carbon monoxide and hydrocarbons can be limited by more combustion efficiency. Currently, four general techniques or modifications for the control of nitrogen oxides are being investigated: combustion modification, fuel modification, furnace design and flue gas treatment. Several of these techniques are presently being applied to large utility boilers, but their applicability to process heaters has not been established.^{2, 14}

9.1.2.8 Compressor Engines - Many older refineries run high pressure compressors with reciprocating and gas turbine engines fired with natural gas. Natural gas has usually been a cheap, abundant source of energy. Examples of refining units operating at high pressure include hydrodesulfurization, isomerization, reforming and hydrocracking. Internal combustion engines are less reliable and harder to maintain than steam engines or electric motors. For this reason, and because of increasing natural gas costs, very few such units have been installed in the last few years.

The major source of emissions from compressor engines is combustion products in the exhaust gas. These emissions include carbon monoxide, hydrocarbons, nitrogen oxides, aldehydes and ammonia. Sulfur oxides may also be present, depending on the sulfur content of the natural gas. All these emissions are significantly higher in exhaust of reciprocating engines than from turbine engines.

The major emission control technique applied to compressor engines is carburetion adjustment similar to that applied on automobiles. Catalyst systems similar to those applied to automobiles may also be effective in reducing emissions, but their use has not been reported.

9.1.2.9 Sweetening - Sweetening of distillates is accomplished by the conversion of mercaptans to alkyl disulfides in the presence of a catalyst. Conversion may be followed by an extraction step for the removal of the alkyl disulfides. In the conversion process, sulfur is added to the sour distillate with a small amount of caustic and air. The mixture is then passed upward through a fixed bed catalyst counter to a flow of caustic entering at the top of the vessel. In the conversion and extraction process, the sour distillate is washed with caustic and then is contacted in the extractor with a solution of catalyst and

Table 9.1-2. FUGITIVE EMISSION FACTORS FOR PETROLEUM REFINERIES^a

Emission Source	Process Stream Type	Emission Factor Units	Emission Factors		Applicable Control Technology	Emission Factor Rating
			Uncontrolled Emissions	Controlled Emissions		
Pipeline valves ^d	II	lb/hr-source	0.039 (0.020 - 0.110)	NA	Monitoring and maintenance program	A
		kg/day-source	0.64 (0.32 - 1.19)			
	III	"	0.024 (0.017 - 0.036)	NA		A
		"	0.26 (0.18 - 0.39)			
	IV	"	0.0005 (0.0002 - 0.0015)	NA		A
Open ended valves ^{d,e}		"	0.005 (0.002 - 0.016)	NA	Installation of cap or plug on open end of valve/line	A
		"	0.05 (0.017 - 0.17)			
	V	"	0.018 (0.007 - 0.045)	NA		A
		"	0.20 (0.08 - 0.49)			
	I	"	0.00054 (0.0002 - 0.0023)	NA		A
Flanges ^d	I	"	0.0061 (0.002 - 0.027)		Monitoring and maintenance program	A
Pump seals ^d	III	"	0.25 (0.16 - 0.37)	NA	Mechanical seals, dual seals, purged seals, monitoring and maintenance program, controlled degassing vent	A
		"	2.7 (1.7 - 4.0)			
	IV	"	0.046 (0.019 - 0.11)	NA		A
Compressor seals ^d		"	0.50 (0.21 - 1.2)		Mechanical seals, dual seals, purged seals, monitoring and maintenance program, controlled degassing vent	A
	II	"	1.4 (0.66 - 2.9)	NA		A
		"	15 (7.1 - 31)			
Process drains ^d		"	0.11 (0.05 - 0.23)	NA	Traps and covers	A
		"	1.2 (0.5 - 2.5)			
	I	"	0.070 (0.023 - 0.20)	NA		A
Pressure vessel relief valves (gas service) ^{d,f}		"	0.76 (0.25 - 2.2)		Rupture disks upstream of relief valves and/or venting to a flare	A
	II	"	0.36 (0.10 - 1.3)	Negligible		A
Cooling towers		lb/10 ⁶ gal cooling water	6	0.70	Minimization of hydrocarbon leaks into cooling water system. Monitoring of cooling water for hydrocarbons	D
		kg/10 ⁶ liters cooling water	0.7	0.083		
		lb/10 ³ bbl refinery feed ^g	10	1.2		
		kg/10 ³ liters refinery feed	0.03	0.004		
		lb/10 ³ gal wastewater	5	0.2		
Oil/water separators		kg/10 ³ liter waste water	0.6	0.024	Covered separators and/or vapor recovery systems	D
		lb/10 ³ bbl refinery feed	200	10		
		kg/10 ³ liters refinery feed	0.6	0.03		
		lb/10 ³ gal wastewater	5	0.2		
Storage		See Section 4.3				
Loading		See Section 4.4				

^aData from References 2, 4, 12 and 13 except as noted. Overall, less than 1% by weight of the total VOC emissions are methane.

NA = Not Available.

^bThe volatility and hydrogen content of the process streams have a substantial effect on the emission rate of some fugitive emission sources. The stream identification numerals and group names and descriptions are:

Stream Identification Numeral	Stream Name	Stream Group Description
I	All streams	All streams
II	Gas streams	Hydrocarbon gas/vapor at process conditions (containing less than 50% hydrogen, by volume)
III	Light liquid and gas/liquid streams	Liquid or gas/liquid stream with a vapor pressure greater than that of kerosene (> 0.1 psia @ 100°F or 689 Pa @ 38°C), based on the most volatile class present at > 20% by volume
IV	Heavy liquid streams	Liquid stream with a vapor pressure equal to or less than that of kerosene (< 0.1 psia @ 100°F or 689 Pa @ 38°C), based on the most volatile class present at > 20% by volume
V	Hydrogen streams	Gas streams containing more than 50% hydrogen by volume

^cNumbers in parentheses are the upper and lower bounds of the 95% confidence interval for the emission factor.

^dData from Reference 17.

^eThe downstream side of these valves is open to the atmosphere. Emissions are through the valve seat of the closed valve.

^fEmission factor for relief valves in gas service is for leakage, not for emissions caused by vessel pressure relief.

^gRefinery rate is defined as the crude oil feed rate to the atmospheric distillation column.

caustic. The extracted distillate is then contacted with air to convert mercaptans to disulfides. After oxidation, the distillate is settled, inhibitors are added, and the distillate is sent to storage. Regeneration is accomplished by mixing caustic from the bottom of the extractor with air and then separating the disulfides and excess air.

The major emission problem is hydrocarbons from contact between the distillate product and air in the "air blowing" step. These emissions are related to equipment type and configuration, as well as to operating conditions and maintenance practices.⁴

9.1.2.10 Asphalt Blowing - The asphalt blowing process polymerizes asphaltic residual oils by oxidation, increasing their melting temperature and hardness to achieve an increased resistance to weathering. The oils, containing a large quantity of polycyclic aromatic compounds (asphaltic oils), are oxidized by blowing heated air through a heated batch mixture or, in continuous process, by passing hot air counter-current to the oil flow. The reaction is exothermic, and quench steam is sometimes needed for temperature control. In some cases, ferric chloride or phosphorus pentoxide is used as a catalyst to increase the reaction rate and to impart special characteristics to the asphalt.

Air emissions from asphalt blowing are primarily hydrocarbon vapors vented with the blowing air. The quantities of emissions are small because of the prior removal of volatile hydrocarbons in the distillation units, but the emissions may contain hazardous polynuclear organics. Emissions are 60 pounds per ton of asphalt.¹³ Emissions from asphalt blowing can be controlled to negligible levels by vapor scrubbing, incineration, or both^{4, 13}

9.1.3 Fugitive Emissions and Controls

Fugitive emission sources are generally defined as volatile organic compound (VOC) emission sources not associated with a specific process but scattered throughout the refinery. Fugitive emission sources include valves of all types, flanges, pump and compressor seals, process drains, cooling towers, and oil/water separators. Fugitive VOC emissions are attributable to the evaporation of leaked or spilled petroleum liquids and gases. Normally, control of fugitive emissions involves minimizing leaks and spills through equipment changes, procedure changes, and improved monitoring, housekeeping and maintenance practices. Controlled and uncontrolled fugitive emission factors for the following sources are listed in Table 9.1-2.

- valves (pipeline, open ended, vessel relief)
- flanges
- seals (pump, compressor)
- process drains
- oil/water separators (wastewater treatment)
- storage
- transfer operations
- cooling towers

9.1.3.1 Valves, Flanges, Seals and Drains - For these sources, a very high correlation has been found between mass emission rates and the type of stream service in which the sources are employed. Except for compressed gases, streams are classified into one of three stream groups, (1) gas/vapor streams, (2) light liquid/two phase streams, and (3) kerosene and heavier liquid streams. Gases passing through compressors are classified as either hydrogen or hydrocarbon service. It is found that sources in gas/vapor stream service have higher emission rates than those in heavier stream service. This trend is especially pronounced for valves and pump seals. The size of sources like valves, flanges, pump seals, compressor seals, relief valves and process drains does not affect the leak rates.¹⁷ The emission factors are independent of process unit or refinery throughput.

Emission factors are given for compressor seals in each of the two gas service classifications. Valves, because of their number and relatively high emission factor, are the major emission source among the source types. This conclusion is based on an analysis of a hypothetical refinery coupled with the emission rates. The total quantity of fugitive VOC emissions in a typical oil refinery with a capacity of 330,000 barrels (52,500 m³) per day is estimated as 45,000 pounds (20.4 MT) per day. See Table 9.1-3.

9.1.3.2 Storage - All refineries have a feedstock and product storage area, termed a "tank farm", which provides surge storage capacity to assure smooth, uninterrupted refinery operations. Individual storage tank capacities range from less than 1000 barrels to more than 500,000 barrels (160 - 79,500 m³). Storage tank designs, emissions and emission control technologies are discussed in detail in Section 4.3.

9.1.3.3 Transfer Operations - Although most refinery feedstocks and products are transported by pipeline, some are transported by trucks, rail cars and marine vessels. They are transferred to and from these transport vehicles in the refinery tank farm area by specialized pumps and piping systems. The emissions from transfer operations and applicable emission control technology are discussed in much greater detail in Section 4.4.

9.1.3.4 Wastewater Treatment Plant - All refineries employ some form of wastewater treatment so water effluents can safely be returned to the environment or reused in the refinery. The design of wastewater treatment plants is complicated by the diversity of refinery pollutants, including oil, phenols, sulfides, dissolved solids, and toxic chemicals. Although the wastewater treatment processes employed by refineries vary greatly, they generally include neutralizers, oil/water separators, settling chambers, clarifiers, dissolved air flotation systems, coagulators, aerated lagoons, and activated sludge ponds. Refinery water effluents are collected from various processing units and are conveyed through sewers and ditches to the wastewater treatment plant. Most of the wastewater treatment occurs in open ponds and tanks.

The main components of atmospheric emissions from wastewater treatment plants are fugitive VOC and dissolved gases that evaporate from the surfaces of wastewater residing in open process drains, wastewater separators, and wastewater ponds (Table 9.1-2). Treatment processes that involve extensive contact of wastewater and air, such as aeration ponds and dissolved air flotation, have an even greater potential for atmospheric emissions.

The control of wastewater treatment plant emissions involves covering wastewater systems where emission generation is greatest (such as covering American Petroleum Institute separators and settling basins) and removing dissolved gases from wastewater streams with sour water strippers and phenol recovery units prior to their contact with the atmosphere. These control techniques potentially can achieve greater than 90 percent reduction of wastewater system emissions.¹³

TABLE 9.1-3. FUGITIVE VOC EMISSIONS FROM AN OIL REFINERY¹⁷

Source	Number	VOC Emissions	
		lb/day	kg/day
Valves	11,500	6,800	3,084
Flanges	46,500	600	272
Pump Seals	350	1,300	590
Compressors	70	1,100	499
Relief Valves	100	500	227
Drains	650	1,000	454
Cooling Towers ^a	-	1,600	726
Oil/Water Separators (uncovered) ^a	-	32,100	14,558
TOTAL		45,000	20,408

^aEmissions from the cooling towers and oil/water separators are based on limited data. EPA is currently involved in further research to provide better data on wastewater system fugitive emissions.

9.1.3.5 Cooling Towers - Cooling towers are used extensively in refinery cooling water systems to transfer waste heat from the cooling water to the atmosphere. The only refineries not employing cooling towers are those with once-through cooling. The increasing scarcity of large water supplies required for once-through cooling is contributing to the disappearance of that form of refinery cooling. In the cooling tower, warm cooling water returning from refinery processes is contacted with air by cascading through packing. Cooling water circulation rates for refineries commonly range from 0.3 to 3.0 gallons (1.1 - 11.0 liters) per minute per barrel per day of refinery capacity.^{2,16}

Atmospheric emissions from the cooling tower consist of fugitive VOC and gases stripped from the cooling water as the air and water come into contact. These contaminants enter the cooling water system from

leaking heat exchangers and condensers. Although the predominant contaminant in cooling water is VOC, dissolved gases such as hydrogen sulfide and ammonia may also be found (Table 9.1-2).^{2,4,17}

Control of cooling tower emissions is accomplished by reducing contamination of cooling water through the proper maintenance of heat exchangers and condensers. The effectiveness of cooling tower controls is highly variable, depending on refinery configuration and existing maintenance practices.⁴

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10.1 CHEMICAL WOOD PULPING

10.1.1 General

Chemical wood pulping involves the extraction of cellulose from wood by dissolving the lignin that binds the cellulose fibers together. The four processes principally used in chemical pulping are kraft, sulfite, neutral sulfite semichemical (NSSC), and soda. The first three display the greatest potential for causing air pollution. The kraft process alone accounts for over 80 percent of the chemical pulp produced in the United States. The choice of pulping process is determined by the desired product, by the wood species available, and by economic considerations.

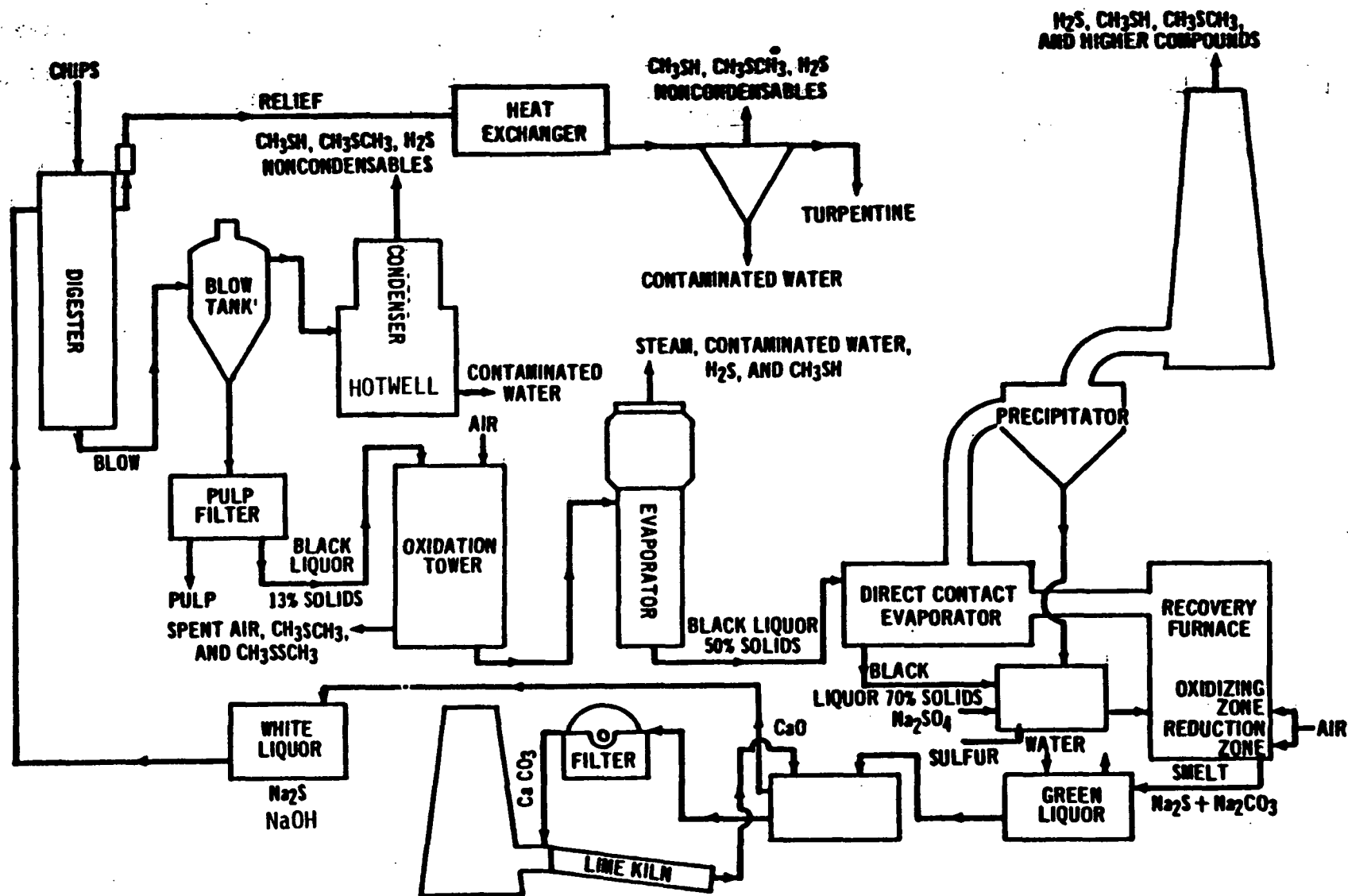
10.1.2 Kraft Pulping

Process Description¹ - The kraft pulping process (See Figure 10.1-1) involves the digesting of wood chips at elevated temperature and pressure in "white liquor", which is a water solution of sodium sulfide and sodium hydroxide. The white liquor chemically dissolves the lignin that binds the cellulose fibers together.

There are two types of digester systems, batch and continuous. Most kraft pulping is done in batch digesters, although the more recent installations are of continuous digesters. In a batch digester, when cooking is complete, the contents of the digester are transferred to an atmospheric tank usually referred to as a blow tank. The entire contents of the blow tank are sent to pulp washers, where the spent cooking liquor is separated from the pulp. The pulp then proceeds through various stages of washing, and possibly bleaching, after which it is pressed and dried into the finished product. The "blow" of the digester does not apply to continuous digester systems.

The balance of the kraft process is designed to recover the cooking chemicals and heat. Spent cooking liquor and the pulp wash water are combined to form a weak black liquor which is concentrated in a multiple effect evaporator system to about 55 percent solids. The black liquor is then further concentrated to 65 percent solids in a direct contact evaporator, by bringing the liquor into contact with the flue gases from the recovery furnace, or in an indirect contact concentrator. The strong black liquor is then fired in a recovery furnace. Combustion of the organics dissolved in the black liquor provides heat for generating process steam and for converting sodium sulfate to sodium sulfide. Inorganic chemicals present in the black liquor collect as a molten smelt at the bottom of the furnace.

The smelt is dissolved in water to form green liquor, which is transferred to a causticizing tank where quicklime (calcium oxide) is added to convert the solution back to white liquor for return to the digester system. A lime mud precipitates from the causticizing tank, after which it is calcined in a lime kiln to regenerate quicklime.



For process heating, for driving equipment, for providing electric power, etc., many mills need more steam than can be provided by the recovery furnace alone. Thus, conventional industrial boilers that burn coal, oil, natural gas, or bark and wood are commonly used.

Emissions And Controls¹⁻⁷ - Particulate emissions from the kraft process occur largely from the recovery furnace, the lime kiln and the smelt dissolving tank. These emissions are mainly sodium salts, with some calcium salts from the lime kiln. They are caused mostly by carryover of solids and sublimation and condensation of the inorganic chemicals.

Particulate control is provided on recovery furnaces in a variety of ways. In mills with either a cyclonic scrubber or cascade evaporator as the direct contact evaporator, further control is necessary, as these devices are generally only 20 to 50 percent efficient for particulates. Most often in these cases, an electrostatic precipitator is employed after the direct contact evaporator, for an overall particulate control efficiency of from 85 to more than 99 percent. Auxiliary scrubbers may be added at existing mills after a precipitator or a venturi scrubber to supplement older and less efficient primary particulate control devices.

Particulate control on lime kilns is generally accomplished by scrubbers. Electrostatic precipitators have been used in a few mills. Smelt dissolving tanks usually are controlled by mesh pads, but scrubbers can provide further control.

The characteristic odor of the kraft mill is caused by the emission of reduced sulfur compounds, the most common of which are hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, all with extremely low odor thresholds. The major source of hydrogen sulfide is the direct contact evaporator, in which the sodium sulfide in the black liquor reacts with the carbon dioxide in the furnace exhaust. Indirect contact evaporators can significantly reduce the emission of hydrogen sulfide. The lime kiln can also be a potential source of odor, as a similar reaction occurs with residual sodium sulfide in the lime mud. Lesser amounts of hydrogen sulfide are emitted with the noncondensable offgasses from the digesters and multiple effect evaporators.

Methyl mercaptan and dimethyl sulfide are formed in reactions with the wood component, lignin. Dimethyl disulfide is formed through the oxidation of mercaptan groups derived from the lignin. These compounds are emitted from many points within a mill, but the main sources are the digester/blow tank systems and the direct contact evaporator.

Although odor control devices, per se, are not generally found in kraft mills, emitted sulfur compounds can be reduced by process modifications and improved operating conditions. For example, black liquor oxidation systems, which oxidize sulfides into less reactive thiosulfates, can considerably reduce odorous sulfur emissions from the direct contact evaporator, although the vent gases from such systems become minor odor sources themselves. Also, noncondensable odorous gases vented from the digester/blow tank system and multiple effect evaporators can be destroyed by thermal oxidation, usually by passing them through the lime kiln. Efficient operation of the recovery furnace, by avoiding overloading and by maintaining sufficient oxygen, residence time and turbulence, significantly reduces emissions of reduced sulfur compounds from

this source as well. The use of fresh water instead of contaminated condensates in the scrubbers and pulp washers further reduces odorous emissions.

Several new mills have incorporated recovery systems that eliminate the conventional direct contact evaporators. In one system, heated combustion air, rather than fuel gas, provides direct contact evaporation. In another, the multiple effect evaporator system is extended to replace the direct contact evaporator altogether. In both systems, sulfur emissions from the recovery furnace/direct contact evaporator can be reduced by more than 99 percent.

Sulfur dioxide is emitted mainly from oxidation of reduced sulfur compounds in the recovery furnace. It is reported that the direct contact evaporator absorbs about 75 percent of these emissions, and further scrubbing can provide additional control.

Potential sources of carbon monoxide emissions from the kraft process include the recovery furnace and lime kilns. The major cause of carbon monoxide emissions is furnace operation well above rated capacity, making it impossible to maintain oxidizing conditions.

Some nitrogen oxides also are emitted from the recovery furnace and lime kilns, although amounts are relatively small. Indications are that nitrogen oxide emissions are on the order of 0.5 and 1.0 kilograms per air dried megagrams (1 and 2 lb/air dried ton) of pulp produced from the lime kiln and recovery furnace, respectively.⁵⁻⁶

A major source of emissions in a kraft mill is the boiler for generating auxiliary steam and power. The fuels used are coal, oil, natural gas or bark/wood waste. See Chapter 1 for emission factors for boilers.

Table 10.1-1 presents emission factors for a conventional kraft mill. The most widely used particulate control devices are shown, along with the odor reductions through black liquor oxidation and incineration of noncondensable offgases. Tables 10.1-2 through 10.1-7 present cumulative size distribution data and size specific emission factors for particulate emissions from sources within a conventional kraft mill. Uncontrolled and controlled size specific emission factors⁷ are presented in Figures 10.1-2 through 10.1-7. The particle sizes presented are expressed in terms of the aerodynamic diameter.

10.1.3 Acid Sulfite Pulping

Process Description - The production of acid sulfite pulp proceeds similarly to kraft pulping, except that different chemicals are used in the cooking liquor. In place of the caustic solution used to dissolve the lignin in the wood, sulfurous acid is employed. To buffer the cooking solution, a bisulfite of sodium, magnesium, calcium or ammonium is used. A diagram of a typical magnesium base process is shown in Figure 10.1-8.

Digestion is carried out under high pressure and high temperature, in either batch mode or continuous digesters, and in the presence of a sulfurous acid/bisulfite cooking liquid. When cooking is completed, either the digester is discharged at high pressure into a blow pit, or its contents are pumped into a dump tank at a lower pressure. The spent sulfite liquor (also called red liquor) then drains through the bottom of the tank and is treated and discarded,

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10.1-5

TABLE 10.1-1. EMISSION FACTORS FOR KRAFT PULPING^a

EMISSION FACTOR RATING: A

Source	Type of control	Particulate		Sulfur dioxide (SO ₂)		Carbon monoxide (CO)		Hydrogen sulfide (S ^m)		RSH, RSR, RSSR (S ^m)	
		kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Digester relief and blow tank	Untreated ^b	-	-	-	-	-	-	0.02	0.03	0.6	1.2
Brown stock washer	Untreated ^b	-	-	-	-	-	-	0.01	0.02	0.2 ^c	0.4 ^c
Multiple effect evaporator	Untreated ^b	-	-	-	-	-	-	0.55	1.1	0.05	0.1
Recovery boiler and direct evaporator	Untreated ^d	90	180	3.5	7	5.5	11	6 ^e	12 ^e	1.5 ^e	3 ^e
	Venturi scrubber ^f	24	48	3.5	7	5.5	11	6 ^e	12 ^e	1.5 ^e	3 ^e
	ESP	1	2	3.5	7	5.5	11	6 ^e	12 ^e	1.5 ^e	3 ^e
	Auxiliary scrubber	1.5-7.5 ^g	3-15 ^g					6 ^e	12 ^e	1.5 ^e	3 ^e
Noncontact recovery boiler without direct contact evaporator	Untreated	115	230	-	-	5.5	11	0.05 ^h	0.1 ^h	-	-
	ESP	1	2	-	-	5.5	11	0.05 ^h	0.1 ^h	-	-
Smelt dissolving tank	Untreated	3.5	7	0.1	0.2	-	-	0.1 ^j	0.2 ^j	0.15 ^j	0.3 ^j
	Mesh pad	0.5	1	0.1	0.2	-	-	0.1 ^j	0.2 ^j	0.15 ^j	0.3 ^j
	Scrubber	0.1	0.2	-	-	-	-	0.1 ^j	0.2 ^j	0.15 ^j	0.3 ^j
Lime kiln	Untreated	28	56	0.15	0.3	0.05	0.1	0.25 ^m	0.5 ^m	0.1 ^m	0.2 ^m
	Scrubber or ESP	0.25	0.5	-	-	0.05	0.1	0.25 ^m	0.5 ^m	0.1 ^m	0.2 ^m
Turpentine condenser	Untreated	-	-	-	-	-	-	0.005	.01	0.25	0.5
Miscellaneous ⁿ	Untreated	-	-	-	-	-	-	-	-	0.25	0.5

^aReferences 8-10. Factors expressed in unit weight of air dried unbleached pulp (ADP). RSH = Methyl mercaptan. RSR = Dimethyl sulfide. RSSR = Dimethyl disulfide. ESP = Electrostatic precipitator. Dash = No data.

^bIf noncondensable gases from these sources are vented to lime kiln, recovery furnace or equivalent, the reduced sulfur compounds are destroyed.

^cApply with system using condensate as washing medium. When using fresh water, emissions are 0.05 (0.1).

^dApply when cyclonic scrubber or cascade evaporator is used for direct contact evaporation, with no further controls.

^eUsually reduced by 50% with black liquor oxidation and can be cut 95 - 99% when oxidation is complete and recovery furnace is operated optimally.

^fApply when venturi scrubber is used for direct contact evaporation, with no further controls.

^gUse 7.5 (15) when auxiliary scrubber follows venturi scrubber, and 1.5 (3) when it follows ESP.

^hApply when recovery furnace is operated optimally to control total reduced sulfur (TRS) compounds.

ⁱUsually reduced to 0.01 g/kg (0.02 lb/ton) ADP when water low in sulfides is used in smelt dissolving tank and associated scrubber.

^mUsually reduced to 0.015 g/kg (0.03 lb/ton) ADP with efficient mud washing, optimal kiln operation and added caustic in scrubbing water. With only efficient mud washing and optimal process control, TRS compounds reduced to 0.04 g/kg (0.08 lb/ton) ADP.

ⁿIncludes knotters vents, brownstock seal tanks, etc. When black liquor oxidation is included, emissions are 0.3 (0.6).

TABLE 10.1-2. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR A RECOVERY BOILER WITH A DIRECT CONTACT EVAPORATOR AND AN ESP^a

EMISSION FACTOR RATING: C

Particle size (μm)	Cumulative mass % \leq stated size		Cumulative emission factor (kg/Mg of air dried pulp)	
	Uncontrolled	Controlled	Uncontrolled	Controlled
15	95.0	-	86	-
10	93.5	-	84	-
6	92.2	68.2	83	0.7
2.5	83.5	53.8	75	0.5
1.25	56.5	40.5	51	0.4
1.00	45.3	34.2	41	0.3
0.625	26.5	22.2	24	0.2
Total	100	100	90	1.0

^aReference 7. Dash = no data.

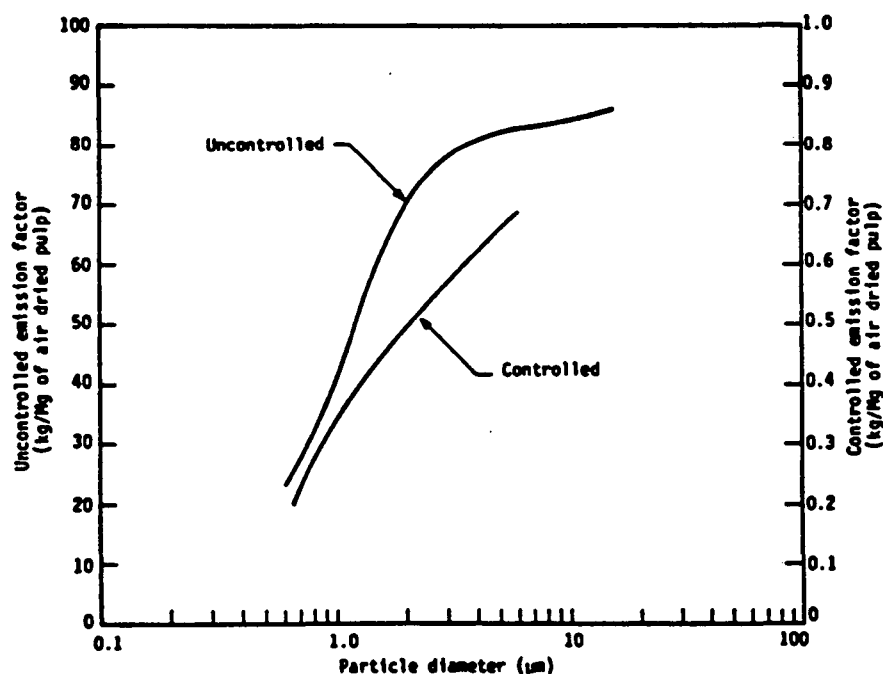


Figure 10.1-2. Cumulative particle size distribution and size specific emission factors for recovery boiler with direct contact evaporator and ESP.

TABLE 10.1-3. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR A RECOVERY BOILER WITHOUT A DIRECT CONTACT EVAPORATOR BUT WITH AN ESP^a

EMISSION FACTOR RATING: C

Particle size (um)	Cumulative mass % ≤ stated size		Cumulative emission factor (kg/Mg of air dried pulp)	
	Uncontrolled	Controlled	Uncontrolled	Controlled
15	-	78.8	-	0.8
10	-	74.8	-	0.7
6	-	71.9	-	0.7
2.5	78.0	67.3	90	0.6
1.25	40.0	51.3	46	0.5
1.00	30.0	42.4	35	0.4
0.625	17.0	29.6	20	0.3
Total	100	100	115	1.0

^aReference 7. Dash = no data.

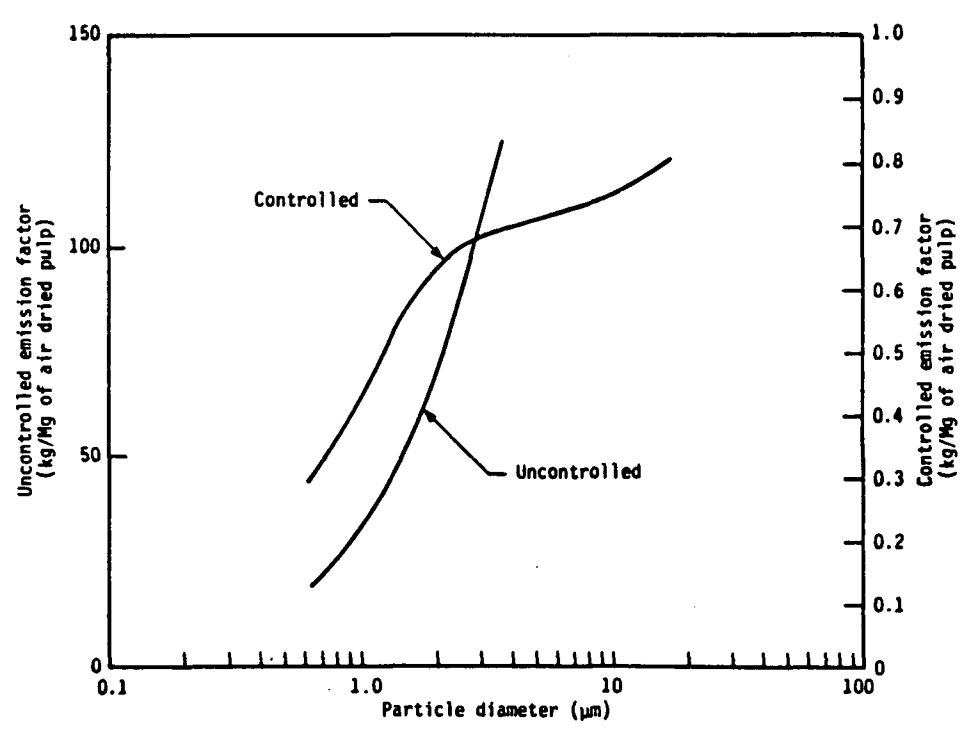


Figure 10.1-3. Cumulative particle size distribution and size specific emission factors for recovery boiler without direct contact evaporator but with ESP.

TABLE 10.1-4. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR A LIME KILN WITH A VENTURI SCRUBBER^a

EMISSION FACTOR RATING: C

Particle size (μm)	Cumulative mass % < stated size		Cumulative emission factor (kg/Mg of air dried pulp)	
	Uncontrolled	Controlled	Uncontrolled	Controlled
15	27.7	98.9	7.8	0.24
10	16.8	98.3	4.7	0.24
6	13.4	98.2	3.8	0.24
2.5	10.5	96.0	2.9	0.24
1.25	8.2	85.0	2.3	0.21
1.00	7.1	78.9	2.0	0.20
0.625	3.9	54.3	1.1	0.14
Total	100	100	28.0	0.25

^aReference 7.

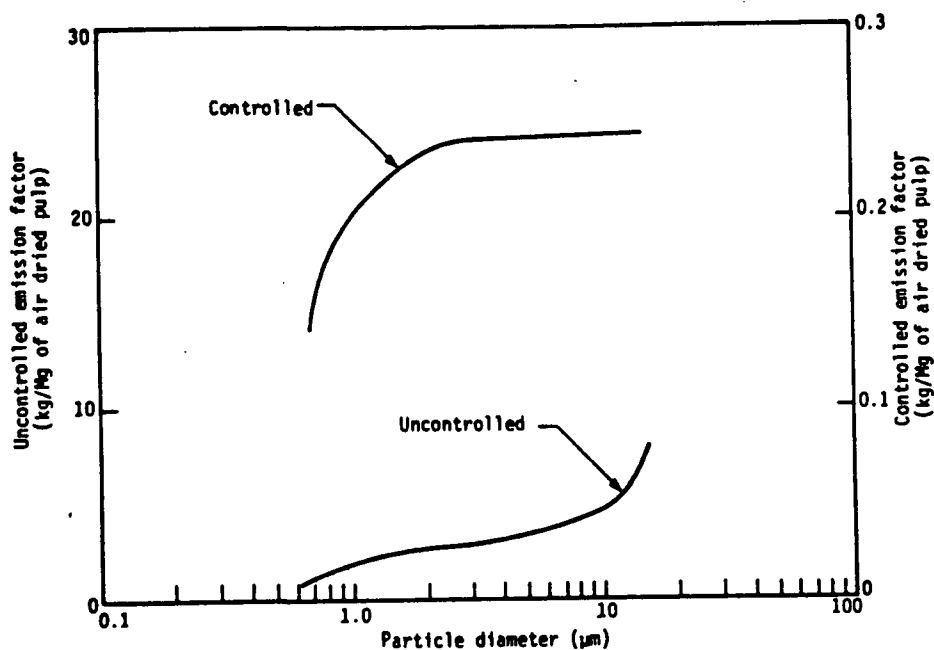


Figure 10.1-4. Cumulative particle size distribution and size specific emission factors for lime kiln with venturi scrubber.

TABLE 10.1-5. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR A LIME KILN WITH AN ESP^a

EMISSION FACTOR RATING: C

Particle size (μm)	Cumulative mass % < stated size		Cumulative emission factor (kg/Mg of air dried pulp)	
	Uncontrolled	Controlled	Uncontrolled	Controlled
15	27.7	91.2	7.8	0.23
10	16.8	88.5	4.7	0.22
6	13.4	86.5	3.8	0.22
2.5	10.5	83.0	2.9	0.21
1.25	8.2	70.2	2.3	0.18
1.00	7.1	62.9	2.0	0.16
0.625	3.9	46.9	1.1	0.12
Total	100	100	28.0	0.25

^aReference 7.

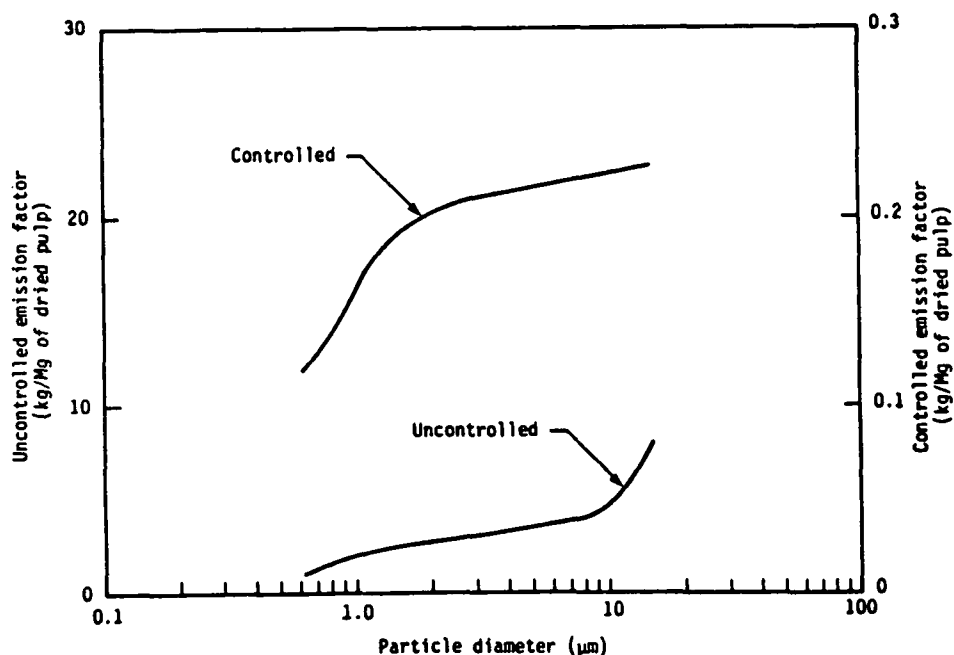


Figure 10.1-5. Cumulative particle size distribution and size specific emission factors for lime kiln with ESP.

TABLE 10.1-6. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR A SMELT DISSOLVING TANK WITH A PACKED TOWER^a

EMISSION FACTOR RATING: C

Particle size (μm)	Cumulative mass % \leq stated size		Cumulative emission factor (kg/Mg of air dried pulp)	
	Uncontrolled	Controlled	Uncontrolled	Controlled
15	90.0	95.3	3.2	0.48
10	88.5	95.3	3.1	0.48
6	87.0	94.3	3.0	0.47
2.5	73.0	85.2	2.6	0.43
1.25	47.5	63.8	1.7	0.32
1.00	40.0	54.2	1.4	0.27
0.625	25.5	34.2	0.9	0.17
Total	100	100	3.5	0.50

^aReference 7.

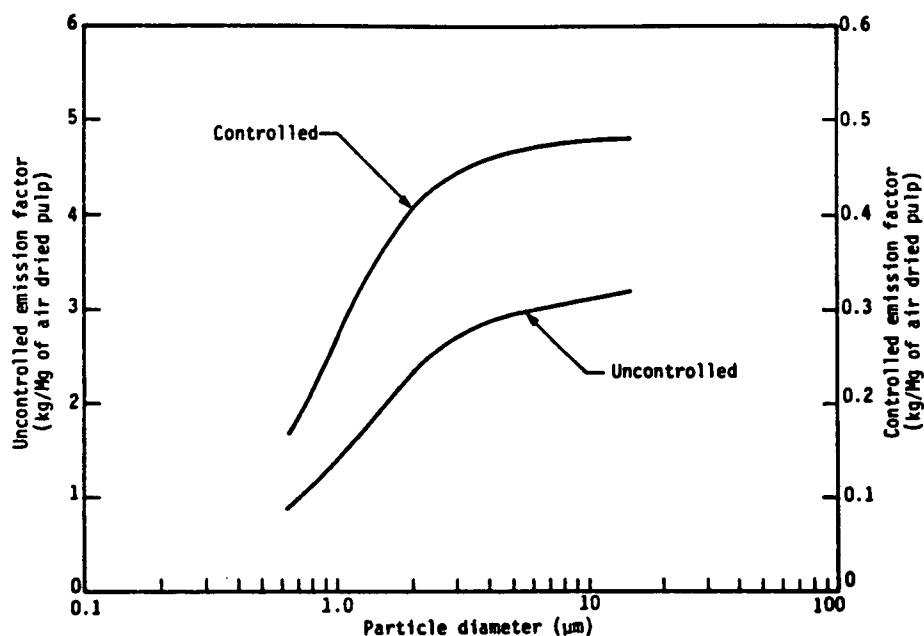


Figure 10.1-6. Cumulative particle size distribution and size specific emission factors for smelt dissolving tank with packed tower.

TABLE 10.1-7. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE SPECIFIC EMISSION FACTORS FOR A SMELT DISSOLVING TANK WITH A VENTURI SCRUBBER^a

EMISSION FACTOR RATING: C

Particle size (um)	Cumulative mass % \leq stated size		Cumulative emission factor (kg/Mg of air dried pulp)	
	Uncontrolled	Controlled	Uncontrolled	Controlled
15	90.0	89.9	3.2	0.09
10	88.5	89.5	3.1	0.09
6	87.0	88.4	3.0	0.09
2.5	73.0	81.3	2.6	0.08
1.25	47.5	63.5	1.7	0.06
1.00	54.0	54.7	1.4	0.06
0.625	25.5	38.7	0.9	0.04
Total	100	100	3.5	0.09

^aReference 7.

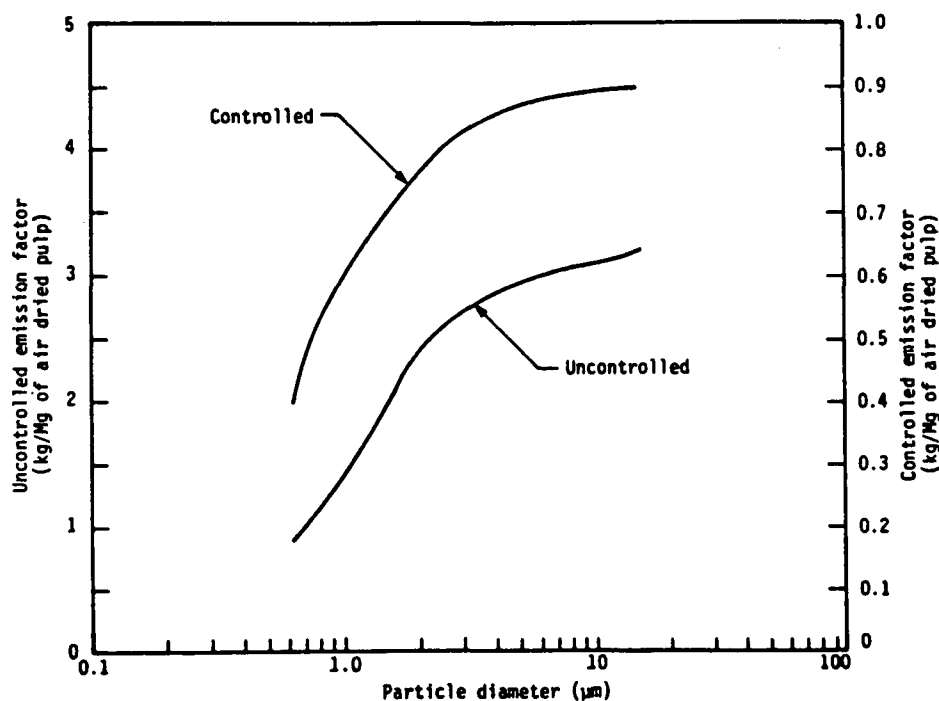


Figure 10.1-7. Cumulative particle size distribution and size specific emission factors for smelt dissolving tank with venturi scrubber.

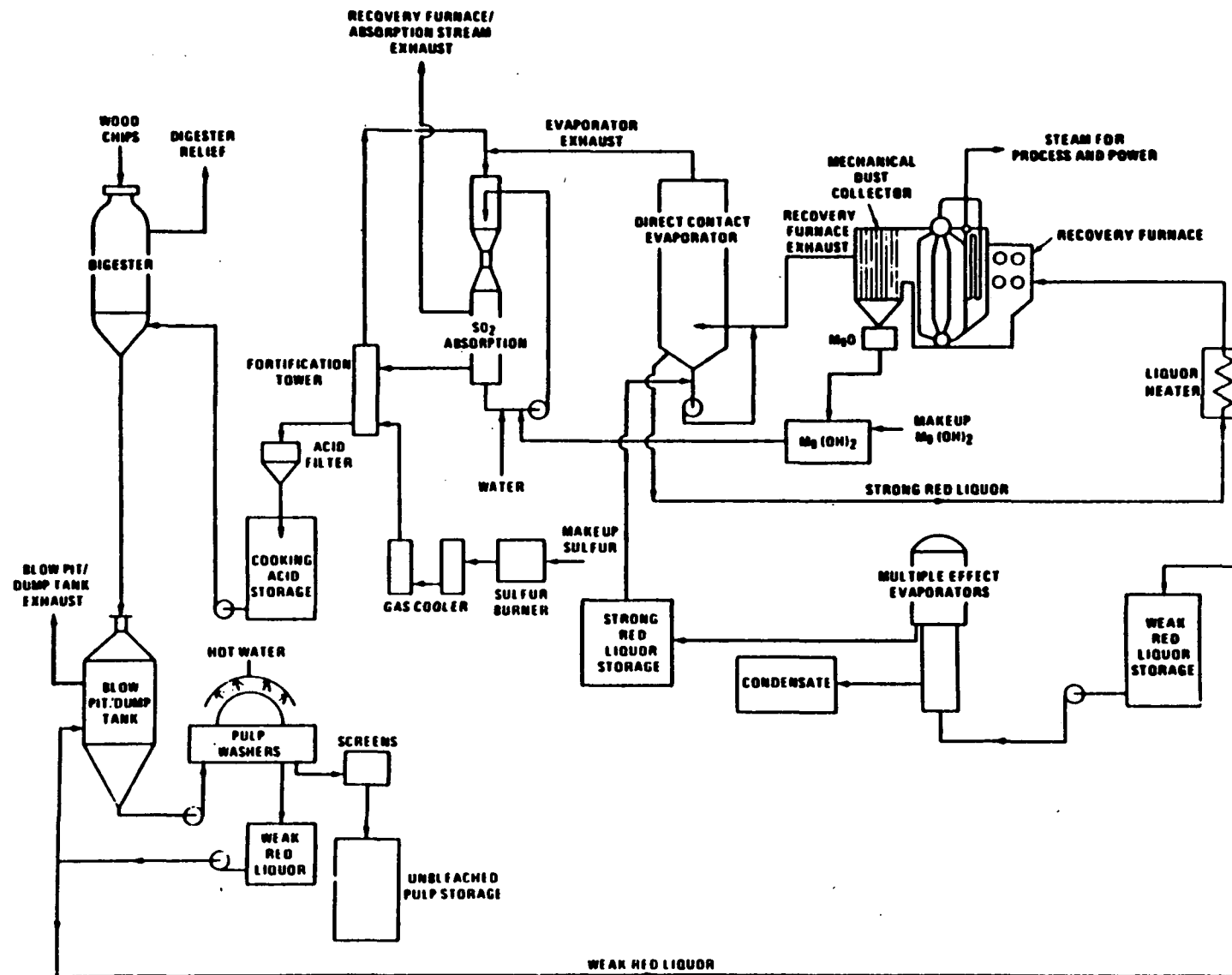


Figure 10.1-8. Simplified process flow diagram of magnesium-base process employing chemical and heat recovery.

incinerated, or sent to a plant for recovery of heat and chemicals. The pulp is then washed and processed through screens and centrifuges to remove knots, bundles of fibers and other material. It subsequently may be bleached, pressed and dried in papermaking operations.

Because of the variety of cooking liquor bases used, numerous schemes have evolved for heat and/or chemical recovery. In calcium base systems, found mostly in older mills, chemical recovery is not practical, and the spent liquor is usually discharged or incinerated. In ammonium base operations, heat can be recovered by combusting the spent liquor, but the ammonium base is thereby consumed. In sodium or magnesium base operations, the heat, sulfur and base all may be feasibly recovered.

If recovery is practiced, the spent (weak) red liquor (which contains more than half of the raw materials as dissolved organic solids) is concentrated in a multiple effect evaporator and a direct contact evaporator to 55 to 60 percent solids. This strong liquor is sprayed into a furnace and burned, producing steam to operate the digesters, evaporators, etc. and to meet other power requirements.

When magnesium base liquor is burned, a flue gas is produced from which magnesium oxide is recovered in a multiple cyclone as fine white power. The magnesium oxide is then water slaked and is used as circulating liquor in a series of venturi scrubbers, which are designed to absorb sulfur dioxide from the flue gas and to form a bisulfite solution for use in the cook cycle. When sodium base liquor is burned, the inorganic compounds are recovered as a molten smelt containing sodium sulfide and sodium carbonate. This smelt may be processed further and used to absorb sulfur dioxide from the flue gas and sulfur burner. In some sodium base mills, however, the smelt may be sold to a nearby kraft mill as raw material for producing green liquor.

If liquor recovery is not practiced, an acid plant is necessary of sufficient capacity to fulfill the mill's total sulfite requirement. Normally, sulfur is burned in a rotary or spray burner. The gas produced is then cooled by heat exchangers and a water spray and is then absorbed in a variety of different scrubbers containing either limestone or a solution of the base chemical. Where recovery is practiced, fortification is accomplished similarly, although a much smaller amount of sulfur dioxide must be produced to make up for that lost in the process.

Emissions And Controls¹¹ - Sulfur dioxide is generally considered the major pollutant of concern from sulfite pulp mills. The characteristic "kraft" odor is not emitted because volatile reduced sulfur compounds are not products of the lignin/bisulfite reaction.

A major SO₂ source is the digester and blow pit (dump tank) system. Sulfur dioxide is present in the intermittent digester relief gases, as well as in the gases given off at the end of the cook when the digester contents are discharged into the blow pit. The quantity of sulfur dioxide evolved and emitted to the atmosphere in these gas streams depends on the pH of the cooking liquor, the pressure at which the digester contents are discharged, and the effectiveness of the absorption systems employed for SO₂ recovery. Scrubbers can be installed that reduce SO₂ from this source by as much as 99 percent.

Another source of sulfur dioxide emissions is the recovery system. Since magnesium, sodium, and ammonium base recovery systems all use absorption systems to recover SO_2 generated in recovery furnaces, acid fortification towers, multiple effect evaporators, etc., the magnitude of SO_2 emissions depends on the desired efficiency of these systems. Generally, such absorption systems recover better than 95 percent of the sulfur so it can be reused.

The various pulp washing, screening, and cleaning operations are also potential sources of SO_2 . These operations are numerous and may account for a significant fraction of a mill's SO_2 emissions if not controlled.

The only significant particulate source in the pulping and recovery process is the absorption system handling the recovery furnace exhaust. Ammonium base systems generate less particulate than do magnesium or sodium base systems. The combustion productions are mostly nitrogen, water vapor and sulfur dioxide.

Auxiliary power boilers also produce emissions in the sulfite pulp mill, and emission factors for these boilers are presented in Chapter 1.

Table 10.1-8 contains emission factors for the various sulfite pulping operations.

10.1.4 Neutral Sulfite Semichemical (NSSC) Pulping

Process Description^{9, 12-14} - In this method, wood chips are cooked in a neutral solution of sodium sulfite and sodium carbonate. Sulfite ions react with the lignin in wood, and the sodium bicarbonate acts as a buffer to maintain a neutral solution. The major difference between all semichemical techniques and those of kraft and acid sulfite processes is that only a portion of the lignin is removed during the cook, after which the pulp is further reduced by mechanical disintegration. This method achieves yields as high as 60 to 80 percent, as opposed to 50 to 55 percent for other chemical processes.

The NSSC process varies from mill to mill. Some mills dispose of their spent liquor, some mills recover the cooking chemicals, and some, when operated in conjunction with kraft mills, mix their spent liquor with the kraft liquor as a source of makeup chemicals. When recovery is practiced, the involved steps parallel those of the sulfite process.

Emissions And Controls^{9,12-14} - Particulate emissions are a potential problem only when recovery systems are involved. Mills that do practice recovery but are not operated in conjunction with kraft operations often utilize fluidized bed reactors to burn their spent liquor. Because the flue gas contains sodium sulfate and sodium carbonate dust, efficient particulate collection may be included for chemical recovery.

A potential gaseous pollutant is sulfur dioxide. Absorbing towers, digester/blower tank system, and recovery furnace are the main sources of SO_2 , with amounts emitted dependent upon the capability of the scrubbing devices installed for control and recovery.

Hydrogen sulfide can also be emitted from NSSC mills which use kraft type recovery furnaces. The main potential source is the absorbing tower, where a

TABLE 10.1-8. EMISSION FACTORS FOR SULFITE PULPING^a

Source	Base	Control	Emission factor ^b				Emission Factor Rating
			Particulate		Sulfur dioxide		
			kg/ADUMg	lb/ADUT	kg/ADUMg	lb/ADUT	
Digester/blow pit or dump tank ^c	All	None	Neg	Neg	5 to 35	10 to 70	C
	MgO	Process changed ^d	Neg	Neg	1 to 3	2 to 6	C
	MgO	Scrubber	Neg	Neg	0.5	1	B
	MgO	Process change and scrubber	Neg	Neg	0.1	0.2	B
	MgO	All exhaust vented through recovery system	Neg	Neg	0	0	A
	NH ₃	Process change	Neg	Neg	12.5	25	D
	NH ₃	Process change and scrubber	Neg	Neg	0.2	0.4	B
	Na	Process change and scrubber	Neg	Neg	1	2	C
	Ca	Unknown	Neg	Neg	33.5	67	C
	Recovery system ^e	MgO	Multicyclone and venturi scrubbers	1	2	4.5	9
NH ₃		Ammonia absorption and mist eliminator	0.35	0.7	3.5	7	B
Na		Sodium carbonate scrubber	2	4	1	2	C
Acid plant ^f	NH ₃	Scrubber	Neg	Neg	0.2	0.3	C
	Na	Unknown ^g	Neg	Neg	0.1	0.2	D
	Ca	Jenssen scrubber	Neg	Neg	4	8	C
Other ^h	All	None	Neg	Neg	6	12	D

^aReference 11. All factors represent long term average emissions. ADUMg = Air dried unbleached megagram. ADUT = Air dried unbleached ton. Neg = negligible.

^bExpressed as kg (lb) of pollutant/air dried unbleached ton (mg) of pulp.

^cFactors represent emissions after cook is completed and when digester contents are discharged into blow pit or dump tank. Some relief gases are vented from digester during cook cycle, but these are usually transferred to pressure accumulators and SO₂ therein reabsorbed for use in cooking liquor. In some mills, actual emissions will be intermittent and for short periods.

^dMay include such measures as raising cooking liquor pH (thereby lowering free SO₂), relieving digester pressure before contents discharge, and pumping out digester contents instead of blowing out.

^eRecovery system at most mills is closed and includes recovery furnace, direct contact evaporator, multiple effect evaporator, acid fortification tower, and SO₂ absorption scrubbers. Generally only one emission point for entire system. Factors include high SO₂ emissions during periodic purging of recovery systems.

^fNecessary in mills with insufficient or nonexistent recovery systems.

^gControl is practiced, but type of system is unknown.

^hIncludes miscellaneous pulping operations such as knotters, washers, screens, etc.

significant quantity of hydrogen sulfite is liberated as the cooking liquor is made. Other possible sources, depending on the operating conditions, include the recovery furnace, and in mills where some green liquor is used in the cooking process, the digester/blow tank system. Where green liquor is used, it is also possible that significant quantities of mercaptans will be produced. Hydrogen sulfide emissions can be eliminated if burned to sulfur dioxide before the absorbing system.

Because the NSSC process differs greatly from mill to mill, and because of the scarcity of adequate data, no emission factors are presented for this process.

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